This is an author generated post-print of the article: Evtyugina M., Vicente E.D., Vicente A.M., Nunes T., Lucarelli F., Calzolai G., Nava S., Alegre C.D., Calvo A.I., Castro A., Fraile R. Oduber F., Cerqueira M., Alves C.A., (2021) Air quality and particulate matter speciation in a beauty salon and surrounding outdoor environment: exploratory study. ATMOSPHERIC POLLUTION RESEARCH, 101174. The final publication is available at https://doi.org/10.1016/j.apr.2021.101174 

# 30 Air quality and particulate matter speciation in a beauty salon and

- 31 surrounding outdoor environment: exploratory study
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#### 49 Abstract

- 50 Beauty salons are considered occupational environments where the staff personnel and clients
- are exposed to high levels of airborne pollutants. In this study, air quality monitoring was
- 52 carried out in Léon, Spain. Temperature, relative humidity, CO<sub>2</sub>, CO and particulate matter
- were continuously monitored inside and outside areas of the salon. PM<sub>10</sub> was simultaneously
- collected onto filters. Volatile organic compounds and carbonyls were sampled inside the salon.
- Indoor  $PM_{10}$  concentrations exceeded the recommended 24-h guideline of  $50 \, \mu g \, m^{-3}$ . A detailed
- 56 PM<sub>10</sub> chemical characterisation included organic and elemental carbon, trace elements, water-
- soluble ions and organic speciation. Indoor vs outdoor ratios of PM<sub>10</sub>, as well as the majority of
- $PM_{10}$ -bound organic compounds, were > 1. During work periods, organic carbon accounted for
- 59  $29.5 \pm 1.8$  and  $16.2 \pm 4.5$  %wt. of PM<sub>10</sub> indoors and outdoors, respectively. More than 200
- 60 individual organic compounds were detected in the PM<sub>10</sub>, including aliphatic alcohols, fatty
- acids, phthalates, glycerol derivatives, fatty acid alkyl esters, phenolic compounds, alkanes and
- 62 polycyclic aromatic hydrocarbons, among others. Many of them are part of formulations widely

- used in hair cosmetics, personal care and cleaning products. Inadequate ventilation, working activities and the use of specific products can greatly contribute to high indoor levels of organic air pollutants. Formaldehyde revealed a cancer risk of  $4.6 \times 10^{-6}$ , higher than the guideline level, suggesting a "possible risk" for workers. The total excess lifetime cancer risk from exposure to multiple compounds was  $9.3 \times 10^{-6}$ , which is lower than the acceptable risk, but not negligible.
- Keywords: Air quality, VOCs, Carbonyls, PM<sub>10</sub>, Elemental composition, Organic
   compounds.

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#### 1. Introduction

73 The US Environment Protection Agency (EPA) ranked indoor air pollution as one of the top five environmental risks to public health. Population spends the bulk of their time in residential 74 75 or non-residential indoor environments, which can have 2–5 times higher pollutant levels than 76 outdoors (EPA, 2015; Jafari et al., 2015; Hadei et al., 2018; Morawska et al., 2013; Pegas et al., 77 2011; Weisel et al., 2008). Furthermore, human exposure to indoor air pollutants may occasionally be more than 100-fold higher when compared to outdoor areas (EPA, 2015). 78 79 Exposure to indoor air pollutants in private and professional environments can lead to a broad range of health problems. Poor indoor air quality can be a common problem in homes (Bentayeb 80 et al., 2015; Du et al., 2020), schools (Kalimeri, et al., 2016; Lucialli et al., 2020; Pegas et al., 81 2011), offices (Guo et al., 2004; Saraga et al., 2014), restaurants (Guo et al., 2004; Lee et al., 82 2001) and other public facilities such as hospitals, elderly care centres, libraries, pharmacies, 83 gymnasiums and museums (Bruno et al., 2008; Śmiełowska et al., 2017). 84 Several hazards have been associated with the hairdressing profession due to the use of a vast 85 array of cosmetic products, many of which have constituents classified as dangerous (Aglan 86 and Mansour, 2020; Czene et al., 2003; EU-OSHA, 2014; Labrèche et al., 2003; Pak et al., 87 2013; Quiros-Alcala et al., 2019). It was recognised that hairdressers are exposed to serious 88 occupational health risks related not only to their work, but also to workspace environment as 89 90 well (Ana et al., 2019; Czene et al., 2003; EU-OSHA, 2014). Particularly, the products and treatment techniques used in beauty salons can put both the salon personnel and customers at 91 92 risk of exposure to hazardous chemicals. Work-related symptoms and diseases such as respiratory symptoms (Al-Marshad et al., 2016; Foss-Skiftesvik et al., 2017; Nemer et al., 93 94 2017), asthma (Dahlgren and Talbott 2018), reproductive disorders (Baste et al., 2008; Henrotin et al., 2015; Pak et al., 2013; Ronda et al., 2009; Rylander et al., 2002) and skin diseases 95

(Hajaghazadeh et al., 2018; Mancini et al., 2018) have been reported for the hairdressers and 96 nail technicians. 97 Indoor air quality (IAQ) in beauty salons can be affected by various contaminants such as 98 ammonia (NH<sub>3</sub>), volatile organic compounds (VOCs) and particulate matter (PM). Pollutant 99 concentrations in beauty salons depend on the type of products used, the area of the facility, the 100 efficiency of air exchange and the number of occupants and treatments (Chang et al., 2018; de 101 102 Gennaro et al., 2014; Goldin et al., 2014). 103 Benzene, toluene, ethylbenzene and xylene (BTEX), commonly found in indoor environments, 104 are well known to be toxic, mutagenic and/or carcinogenic. Health risk assessment studies showed that benzene, ethylbenzene, formaldehyde and acetaldehyde, measured in beauty 105 106 salons, represent a possible cancer risk, while toluene, ethylbenzene and xylene had negligible non-carcinogenic risks (Hadei et al., 2018; Baghani et al., 2018). Formaldehyde has been widely 107 108 reported to cause dermatologic allergic reactions (Kim et al., 2011) and was classified as a probable human carcinogen by the Integrated Risk Information System (IRIS) and as a 109 110 carcinogenic by the International Agency for Research on Cancer (IARC) and by the U.S. National Toxicology Program (NTP) agencies. Polycyclic aromatic hydrocarbons (PAHs), 111 commonly found in particulate matter, were considered as potent carcinogens and associated 112 with lung cancer (WHO, 2010). 113 Hairdressers are chronically exposed to formaldehyde concentrations that meet or exceed 114 current occupational exposure limits in the work environment. These exposures are 115 predominantly associated with the use of products for hair straightening (Aglan and Mansour, 116 2020; Dahlgren and Talbott, 2018; Peteffi et al., 2016; Pexe et al., 2019; Pierce et al., 2011; 117 118 Stewart et al., 2013). Furthermore, cancer risk values for prolonged exposure to benzene and ethylbenzene can be drastically higher than recommended levels (Baghani et. al. 2018). 119 120 Several IAQ and/or exposure assessment studies have been carried out in hairdressing and beauty salons, but most of them assessed a limited number of air pollutants. Ronda et al. (2009) 121 122 examined comfort parameters (air temperature, relative humidity), CO and CO<sub>2</sub> and found low 123 exposure levels for thirty-three VOCs in the working environment of hairdressers. Gennaro et al. (2014) have reported much higher indoor levels in hair salons for several VOCs, including 124 125 oxygenated compounds and terpenes, when compared to outdoor concentrations. Total volatile organic compounds (TVOC) concentration, CO<sub>2</sub> and PM<sub>2.5</sub> were measured in nail salons by 126 127 Goldin et al. (2014). The results of their study demonstrate that TVOCs and PM with aerodynamic diameter less than 2.5 µm (PM<sub>2.5</sub>) exceed typical levels found in residential 128

environments. The concentrations of oxygenated VOCs, CO<sub>2</sub>, formaldehyde and phthalate

esters were measured at hairdressing salons by Chang et al. (2018). They detected higher levels of VOCs and phthalates than what has been monitored in residential areas. Relatively few studies measured airborne particles in beauty salons. Exposure levels of persulphate (S<sub>2</sub>O<sub>8</sub><sup>2-</sup>) containing particles were measured by Mounier-Geyssant et al. (2006) and Nilsson et al. (2015). Shao et al. (2021) characterised indoor PM<sub>2.5</sub> and PM<sub>10</sub> concentrations in hair salons primarily serving a Black/Latino clientele. Their findings suggest that hairdressers could be potentially overexposed to respirable particles during an 8-hour shift based on current occupational exposure limits. Saraga et al. (2014) studied the respirable particle levels in different workplaces and recorded the maximum particle concentration at a hairdresser store. In other studies, performed in beauty salons, total suspended particulate matter (TSP), its respirable sub-fraction (PM<sub>4</sub>) and carbonaceous content (organic and elemental carbon, OC and EC) were simultaneously measured indoors and outdoors (Rogula-Kopiec et al., 2017; 2019). The chemical composition of airborne particles in beauty salons is poorly known. Therefore, there is a need for further research, given that beauty salon staff are exposed to a vast number of airborne chemicals during the whole workday and that the characterisation of the chemical composition of PM is an important factor to establish the relationship between occupational health hazards and IAQ. The main objective of this study was focused on air quality monitoring in a beauty salon in León (Spain) with special emphasis on PM<sub>10</sub>-bound compounds. A detailed characterisation of organic and inorganic components of PM<sub>10</sub> was carried out for the first time. Additionally, comfort parameters and VOC concentrations were evaluated. 

## **2. Methodology**

#### 2.1. Sampling site and strategy

The study was carried out between 20<sup>th</sup> and 24<sup>th</sup> of November 2017 in a hairdresser salon located in the vicinity of a relatively dense traffic avenue in León, Spain. The salon is located in a building nearby the university and is open from Monday to Friday for 10 hours straight. Customers were either regular or occasional, generally of both sexes, with a higher proportion of men. The space layout included a reception/ waiting room at the front, two hairstyling areas, a waxing room and a dispensary room in the back. Most hair care products are mixed in the dispensary where most of hairstyling products are stored. The salon offers a wide range of services including manicures, pedicures, waxing services and hair styling/colouring. The number of clients and the respective type of treatments were monitored for each sampling day (Table S1). There were no heating, ventilation or air conditioning (HVAC) systems inside the working space. Taking into account that the measurement campaign took place in winter, the windows were closed. The door was opened periodically during the entrance and exit of clients.

monitoring were carried out for five working days and one weekend day. The measurements were performed simultaneously inside and outside of the salon during occupancy periods and only in the indoor environment during the non-occupancy period. Airborne PM<sub>1</sub>, PM<sub>2.5</sub> and PM<sub>10</sub> were continuously monitored by a photometric method. Two samplers were used to collect PM<sub>10</sub> onto quartz and Teflon filters for gravimetric analysis and determination of trace elements, water-soluble ions, carbonaceous content, and speciation of organic compounds. The

The sampling design is presented in Table S2. Comfort parameters, CO, CO<sub>2</sub> and PM

monitoring equipment and PM samplers were placed in the centre of the salon. Outdoors, the

equipment was placed about 3 m away from the salon. Considering that the main objective of

this study was focused on chemical composition of PM, VOCs and carbonyl compounds were

sampled only indoors for three working days. Three VOC/carbonyl samples per day, covering

the working hours, were collected.

176 Health risk were assessed according to the methodology established by the United States

177 Environmental Protection Agency (Supporting Information).

178 2.2. Air quality monitoring

179 2.2.1. Comfort parameters, CO, CO<sub>2</sub> and ventilation rate

180 Temperature, relative humidity, CO<sub>2</sub> and CO were continuously monitored with air quality

probes inside (TSI, model 7545) and outside (Gray Wolf®, WolfSense IQ-610) the salon. The

air exchange rate (AER) was estimated by the CO<sub>2</sub> concentration decay method (Alves et al.,

183 2020).

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184 2.2.2. *Volatile organic compounds* 

VOCs for quantitative analysis were collected on tenax/sulphicarb tubes (Gradko) connected to

sampling pumps, which were calibrated to provide a volumetric airflow rate of 50 mL min<sup>-1</sup>.

187 VOC samples were analysed via thermal desorption and gas chromatography-mass

spectrometry (GC-MS) in an accredited laboratory (Gradko International Ltd) following the

methodology established in ISO 16000-6, Part 6.

190 Carbonyls were sampled with Waters Sep-Pak® DNPH-silica cartridges at a flow rate of 2 L

191 min<sup>-1</sup>. The elution of aldehyde derivatives was performed with 3 mL of acetonitrile (Fischer

192 Scientific). The carbonyl-DNPH derivatives were analysed by high performance liquid

chromatography (HPLC). HPLC measurements were carried out with a Jasco PU-980 pump, a

Rheodyne 7125 six-port valve with a 20 μL loop and a Jasco MD-1510 diode array detector.

An isocratic mixture of acetonitrile and water (60:40), with a flow rate of 1.5 mL min<sup>-1</sup>, was

mil min , was

used to separate the 2,4-DNPH on a Supelcosil<sup>TM</sup> LC-18 column (5  $\mu$ m particle size; L  $\times$  I.D.

197  $250 \times 4.6$  mm). Calibration of the analytical system was performed using DNPH-derivatives of

- carbonyl compounds from Supelco. The Statistical Package for Social Sciences (IBM SPSS
- 199 Statistics 27) was used for calculation of Pearson correlation coefficient.
- 200 2.2.3. Particulate matter
- 201 Airborne PM mass concentrations were continuously measured by a laser photometric
- 202 instrument (TSI, DustTrak DRX 8533) in the indoor and outdoor environments,
- simultaneously. These continuous monitoring instruments were operated with 1-min resolution.
- 204 PM<sub>10</sub> samples were collected onto 150 mm quartz fibre filters (Pall Corporation) with two high
- volume air MCV (model CAV-A/mb) instruments, working at a constant flow of 30 m<sup>3</sup> h<sup>-1</sup>.
- 206 PM<sub>10</sub> samples were also collected on Teflon membrane filters (47 mm diameter, Pall
- 207 Corporation) with a TCR TECORA (model 2.004.01) operated at a flow of 2.3 m<sup>3</sup> h<sup>-1</sup>. The
- 208 gravimetric quantification was performed with an analytical balance (Mettler Toledo, XPE105
- 209 DeltaRange®).
- The carbonaceous content (OC and EC) in PM<sub>10</sub> samples (quartz filters) was analysed by a
- 211 thermal optical transmission technique. The method consists of particulate carbon volatilisation
- by means of controlled heating, with subsequent conversion by oxidation to  $CO_2$  for detection.
- 213 The monitoring of the blackening of the filters through light transmittance allows the separation
- of EC formed by OC pyrolysis from the one that was originally in the sample (Pio et al., 2011).
- Two 47 mm diameter punches of each quartz filter were extracted with dichloromethane (125)
- 216 mL, 24 h) and methanol (25 mL for 10 min, two extractions). The total organic extracts were
- 217 concentrated using a Turbo Vap® II concentrator (Biotage) and dried under a nitrogen stream.
- Night sampling filters were extracted all at once, while the indoor and outdoor samples
- 219 collected during the occupancy periods were extracted individually. Each total organic extract
- 220 was separated into five different organic fractions by flash chromatography described in detail
- by Alves et al. (2011). All extracts were analysed by gas chromatography-mass spectrometry
- 222 (GC-MS) with quadrupole. Data were acquired in the electron impact (EI) mode at 70 eV using
- helium as carrier gas at 1.1 mL min<sup>-1</sup>. Aliphatic and polycyclic aromatic hydrocarbons extracts
- were analysed in a Shimadzu QP5050A equipped with a TRB-5MS 30 m  $\times$  0.25 mm  $\times$  0.25  $\mu$ m
- column. The oven temperature program was as follows: 60 °C (1 min), 60–150 °C (10 °C
- 226 min<sup>-1</sup>), 150–290 °C (5 °C min<sup>-1</sup>), 290 °C (30 min). The aliphatic compounds were analysed in
- 227 full scan mode while PAHs were monitored in selected ion mode (SIM). Before
- 228 chromatographic injection, polar organic compounds were derivatised to trimethylsilyl ethers
- by addition of N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA):trimethylchlorosilane
- 230 (TMCS) 99:1 (Supelco) and pyridine containing 2 internal standards: 1-chlorohexadecane
- 231 (Merck) and tetracosane-d<sub>50</sub> (Aldrich). The reaction mixture was heated in an oven at 70 °C for

- 3 h. The GC-MS used for the determination of oxygenated compounds was from Thermo
- Scientific (Trace Ultra, quadrupole DSQ II), equipped with a TRB-5MS 60 m  $\times$  0.25 mm  $\times$
- 0.25 μm column. The oven temperature program was as follows: 60 °C (1 min); 60–150 °C (10
- °C min<sup>-1</sup>), 150–290 °C (5 °C min<sup>-1</sup>), 290 °C (37 min). The silylated compounds were analysed
- in both full scan and selected ion monitoring (SIM) modes.
- 237 After weighing the Teflon filters for PM<sub>10</sub> quantification, one half of each filter was used for
- 238 the determination of the elemental composition by proton-induced X-ray emission (PIXE),
- which enables a non-destructive and simultaneous analysis of elements with atomic number
- above 10 (Lucarelli et al., 2014). The other half of the filter was extracted with Milli-Q water
- by ultrasonic agitation (15+15 min) for ion chromatography analysis. A detailed description of
- the sample preparation method and analytical equipment can be found elsewhere (Vicente et
- 243 al., 2020).
- 244 2.2.4. QC & QA measures
- 245 All monitoring equipment was calibrated prior to use by employing routine calibration
- procedures. The pump flowrate was calibrated before sampling of VOCs using a soap bubble
- 247 glass flow meter. To avoid contamination, the quartz filters were pre-baked at 500 °C for 6 h.
- 248 The GC–MS calibration was performed in six levels (3-50 ppm) by injection of more than a
- 249 hundred authentic standards. Standards and samples were both co-injected with internal
- 250 standards. All chemicals were of analytical reagent grade (Sigma-Aldrich). The limit of
- detection (LOD) and limit of quantification (LOQ) varied from 0.02 to 6.3 and from 0.07 to
- 252 20.8 ng m<sup>-3</sup>, respectively, depending on the compound. Generally, the extraction recovery was
- accomplished based on previous works and varied from 60 to 99% for oxygenated compounds
- and from 38 to 133% for PAHs and phthalates (Vicente et al., 2019). Quality assurance
- 255 procedures also included field blanks for each technique, which were subjected to the same
- analytical procedures, and their concentrations were subtracted from those of real samples.

# 257 3. Results and Discussion

- 258 3.1. Comfort parameters, CO, CO<sub>2</sub> and ventilation rates
- 259 Temperature and relative humidity affect the perception of comfort in an indoor environment
- and are related to one's metabolic heat production, transfer of heat to the environment,
- 261 physiological adjustments and body temperature. For winter, the American Society of Heating,
- 262 Refrigerating and Air-Conditioning Engineers (ASHRAE) indoor environmental guidelines
- recommend maintaining the temperature in the range between 20.3 and 23.9 °C, assuming 50%
- relative humidity. The mean indoor temperature during working hours in the beauty salon was
- $18.7 \pm 0.7$  °C (Table S3). These values do not provide reasonable comfort without special

clothing and could present discomfort to both workers and clients. The relative humidity 266 recorded inside the salon was between 28.6 and 53.2%, which is within the comfort zone: below 267 65% and in the 30-60% range recommended by ASHRAE and EPA, respectively. Carbon 268 dioxide, a by-product of the human metabolism, is widely used as an indicator of IAO and 269 ventilation rate. The mean daily indoor concentration of  $CO_2$  (818  $\pm$  82 ppm) remained within 270 271 the ASHRAE permissible limit of 700 ppm above outdoor CO<sub>2</sub> concentrations. The distribution pattern showed higher CO<sub>2</sub> levels during the day and lower at night (Fig. 1). The indoor CO<sub>2</sub> 272 concentrations correlated linearly with the daily number of clients attending the salon ( $R^2$  = 273 274 0.72). The highest CO<sub>2</sub> concentrations near the ASHRAE permissible level were observed on the 1st day and were related to the maximum number of customers per day. Indoor CO 275 276 concentration levels did not exceed the maximum allowable short-term limit of 9 ppm established by ASHRAE for CO in indoor air. 277

The air exchange rate (AER) values ranged between 0.28 and 0.41 h<sup>-1</sup>, which indicate lack of adequate ventilation. The minimum recommended ventilation rates for acceptable IAQ in beauty and barber shops range from 6 to 10 h<sup>-1</sup> (Engineering ToolBox, 2005). Given that during wintertime airing of the salon can be limited, the installation of heating and ventilation systems could provide the necessary conditions to assure the acceptable thermal comfort and IAQ.

#### 3.2. Volatile organic compounds 283

3.2.1. BTEX 284

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BTEX are commonly the most abundant compounds amongst VOCs found in the indoor 285 environment. Primary indoor sources of BTEX include building materials, fuel combustion, 286 tobacco smoke and consumer products. Combustion of fossil fuels has been pointed out as the 287 288 largest contributor to outdoor air concentrations of these compounds (Bolden et al., 2015). BTEX are referred by the World Health Organisation (WHO) as hazardous air pollutants due 289 290 to their toxicity. WHO classified benzene as a human carcinogen, however, no safe level of exposure has yet been established. Toluene, ethylbenzene and xylenes are also classified as 291 292 potential carcinogens to humans. 293

BTEX levels of the present work were lower than those observed in previous studies (Table 1). Among them, toluene and m,p-xylene showed the highest mean concentrations (Fig. 2). The presence of high indoor concentrations of toluene and xylene isomers can be related to the use of cleaning products and hair sprays containing these compounds as solvents (Rahman and Kim, 2014; Rothe et al., 2011). Benzene and ethylbenzene showed relatively low mean concentrations and were well below the professional exposure limits for Spain (INSHT, 2014).

Higher average concentrations of toluene (up to 816 µg m<sup>-3</sup>), comparable to those measured in

studies involving oil refinery and auto garage workers, were detected in nail salons (Lamplugh et al., 2019). Moradi et al. (2019) found higher average indoor concentrations of BTEX than those in ambient air. They concluded that urinary BTEX concentrations in beauty practitioners were significantly higher than in the control group. The urinary concentrations were associated with BTEX concentrations in the air. Hadei et al. (2018) detected the highest indoor concentration for o-xylene (10-23 µg m<sup>-3</sup>) in large beauty salons. It was concluded that concentrations of benzene and toluene were affected by the number of hair dyeing treatments, while the concentration of xylene was affected by the number of hair styling. Baghani et al. (2018) recorded the highest indoor levels for ethylbenzene and benzene. In their study, the concentration of benzene was significantly influenced by operational conditions (e.g. type of ventilation system, area of salons, the number of people in the salon and number of services). Tsigonia et al. (2010) examined the exposure of workers to VOCs in beauty salons and observed that pollutant levels were influenced by the number of treatments performed, the ventilation, and the number and type of products that were open during the measurements. Ronda et al. (2009) did not observe differences between exposure levels in salons in central and suburban areas of Spain. It was suggested that the exposure was mostly related to hair dye products, highly rich in chemicals, which are extensively used during treatments. Although the BTEX levels in the outdoor air have not been measured, the concentrations monitored outside a cafeteria, located a few meters from the hairdressing salon, in a monitoring campaign carried out at practically the same time (November-December 2017) than that of the present study, can be taken as a comparative reference. In that campaign, outdoor concentrations (µg m<sup>-3</sup>) of 0.6-0.8 (benzene), 1.3-1.6 (toluene), 0.3-0.5 (ethylbenzene), 0.6-1.0 (m-xylene), 0.3-0.4 (p-xylene) and 0.3-0.5 (o-xylene) were obtained (Alves et al., 2020). These values are 2 to 20 times lower than those measured in the hairdressing salon, proving the importance of BTEX emissions from indoor sources.

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### 3.2.2. Formaldehyde and acetaldehyde

Among carbonyl compounds, formaldehyde and acetaldehyde are most frequently identified in indoor environments. Typical indoor sources of these compounds in non-smoking environments include housing and furniture materials, cleaning products such as detergents, disinfectants, softeners, carpet cleaners and shoe products, cosmetics such as liquid soaps, shampoos, nail varnishes and nail hardeners and other consumer items such as insecticides (WHO, 2010). Formaldehyde has been classified as a probable human carcinogen (group B1)

by IRIS and as a human carcinogen (Group 1) by IARC. Acetaldehyde is also considered as a 333 probable human carcinogen (Group B2) by IRIS. 334 In this study, formaldehyde and acetaldehyde presented higher indoor levels than BTEX, with 335 mean concentrations of  $11.5 \pm 3.5$  and  $8.96 \pm 4.6 \,\mu g \, m^{-3}$ , respectively (Fig. 2). Formaldehyde 336 was below the short-term (30-minute) guideline of 100 µg m<sup>-3</sup> recommended by the WHO and 337 below the Short-Term Exposure Limit (STEL) of 46 mg m<sup>-3</sup> recommended by the Spanish 338 National Institute of Safety and Hygiene (INSHT, 2014). Acetaldehyde was also significantly 339 below the STEL of 0.37 mg m<sup>-3</sup> in Spain. The formaldehyde and acetaldehyde outdoor levels 340 measured in the vicinity in another monitoring campaign were, on average, 1.3 µg m<sup>-3</sup> and 341 below the detection limit, respectively (Alves et al., 2020). 342 Highly variable indoor concentrations of carbonyl compounds have been reported in previous 343 studies. Chang et al. (2018) conducted an IAQ study in different areas of 10 hairdressing salons 344 in Taipei (Taiwan), and found accumulation of air pollutants, especially in the working areas. 345 The highest concentration  $(1.04 \times 10^3 \, \mu g \, m^{-3})$  of formaldehyde was observed at the working 346 area, while the lowest concentration (12.4 µg m<sup>-3</sup>) was obtained at the reception area. The 347 authors associated the number of workers, perming treatments and frequency of using 348 formaldehyde releasing products with levels of formaldehyde. Labrèche et al. (2003) reported 349 a mean concentration of formaldehyde of 27 µg m<sup>-3</sup> measured in 26 hairdressing salons in 350 Montreal (Canada). In 6 nail salons in Colorado (USA), formaldehyde average concentrations 351 ranged between 5.32 and 20.6 mg m<sup>-3</sup> (Lamplugh et al., 2019). 352 A higher mean concentration of acetaldehyde (32.6  $\pm$  12.6  $\mu$ g m<sup>-3</sup>) was measured in beauty 353 salons by Hadei et al. (2018), while the formaldehyde concentration was found to be lower 354  $(11.9 \pm 5.9 \,\mu \text{g m}^{-3})$ , being affected by the number of hair styling and nail treatments. The release 355 of formaldehyde into the work environment was predominantly associated with the use of 356 professional hair straightening products (Aglan and Mansour, 2020; Dahlgren and Talbott, 357 2018; Peteffi et al., 2016; Pexe et al., 2019; Pierce et al., 2011; Stewart et al., 2013). Hair 358 straighteners, containing methylene glycol or glyoxylic acid, are capable of releasing 359 formaldehyde when heated during the blow-dry and hot iron application (Dias, 2015). 360 Strong correlations, with high statistical significance, were found between toluene, 361 362 ethylbenzene and xylenes (R<sup>2</sup>>0.76), suggesting that these compounds could have the same origins (Table S4). Formaldehyde was also strongly correlated with ethylbenzene and xylenes 363 (p<0.01). In addition, a significant correlation was obtained between formaldehyde and 364

acetaldehyde ( $R^2 = 0.52$ ), indicating that 52% of formaldehyde and acetaldehyde variations are

366 associated.

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### 3.3. Particulate matter

368 3.3.1.  $PM_{10}$  concentrations

The strong linear relationship between the photometric and gravimetric PM measurements (R<sup>2</sup> 369 = 0.93) showed high agreement between both methods (Fig. S1). The real-time data of PM<sub>10</sub> 370 concentrations collected by the photometric monitors showed strong variations over the 371 sampling period (Fig. 3A). The diurnal maximum and minimum values of PM<sub>10</sub> concentrations 372 measured in the indoor air ranged between 212-1840 µg m<sup>-3</sup> and from 7 to 13 µg m<sup>-3</sup>, 373 respectively. The concentration peaks are usually related to strong short-term emissions from 374 specific sources like use of sprays and hairdryers (Saraga et al., 2014; Van Der Wal et al., 1997). 375 In this study the major indoor peaks of PM<sub>10</sub> that were registered over the sampling days 376 coincided with the drying operation of long hair and the use of hair lacquer sprays. PM 377 378 emissions during drying may be related to the flaking of dead hair cells, as well as the release of products applied to the hair by brushing and drying heat. The turbulence generated by the 379 380 dryer can also lead to the resuspension of particles deposited on surfaces and clothing. Generally, PM<sub>10</sub> peaks occurred after a few minutes (<15 min) the emissions started, while the 381 382 decrease took more than 1 h 30 min after the end of drying/lacquer operation. Other activities 383 such as washing/cutting hair, short time hair drying (<5 min), manicure and sweeping of hair had a substantially lower contribution to the increase of PM<sub>10</sub>. During the night, inside the 384 beauty salon, the PM<sub>10</sub> concentrations dropped drastically ranging from 2 to 19 µg m<sup>-3</sup>. In the 385 first four days, the outdoor concentrations corresponding to occupancy periods were lower (8-386 226 µg m<sup>-3</sup>). The outdoor PM<sub>10</sub> concentration peak (621 µg m<sup>-3</sup>) was observed on the 5<sup>th</sup> day 387 between 11:00 and 12:00, when construction works across the street took place. The 388  $PM_{2.5}/PM_{10}$  indoor ratios represented values between 0.91 and 0.96 (avg = 0.94  $\pm$  0.03) during 389 the sampling period, with the exception of the  $4^{th}$  day (PM<sub>2.5</sub>/PM<sub>10</sub> = 0.63). On average, the 390 ratio of outdoor  $PM_{2.5}/PM_{10}$  was  $0.81 \pm 0.04$  for all sampling days, evidencing the dominance 391 392 of fine-mode particles. From gravimetric measurements, mean indoor  $PM_{10}$  concentrations of 89  $\pm$  39 and 22.8  $\pm$  2.1 393 μg m<sup>-3</sup> were recorded during the occupancy and non-occupancy hours, respectively, while a 394 value of  $50 \pm 12 \,\mu g \, m^{-3}$  was observed outdoors (Fig. 3B). The indoor vs outdoor (I/O) ratio, 395 which is a critical indicator of internal sources, ranged between 0.9 and 4.3 with a mean value 396 of 1.97. The indoor PM<sub>10</sub> concentrations exceeded the 24-h guideline of 50 µg m<sup>-3</sup> 397

- recommended by the WHO. Son et al. (2006) have reported indoor and outdoor concentrations
- of PM<sub>10</sub> of 30.5  $\pm$  25.8 and 31.0  $\pm$  53.6  $\mu$ g m<sup>-3</sup>, respectively, in beauty shops in South Korea.
- Saraga et al. (2014) measured respirable particles in sixteen different working environments
- and recorded the maximum particle concentration (on average 285 µg m<sup>-3</sup>) at a hairdresser store.
- 402 Other study took place in 20 workplaces, including three hair salons, located in Alexandroupolis
- 403 (Greece) and recorded PM<sub>2.5</sub> concentrations between 127 and 171 μg m<sup>-3</sup> (Kogianni et al.,
- 404 2020). Similar mean concentrations of PM<sub>4</sub>, between 92.8-170 and 9.4-105 μg m<sup>-3</sup>, were
- measured by Rogula-Kopiec et al. (2019) inside and outside 4 beauty salons in Silesia (Poland),
- 406 respectively. The corresponding indoor and outdoor mean concentrations of TSP varied from
- 407 136 to 277  $\mu$ g m<sup>-3</sup>. The mean I/O ratios of PM<sub>4</sub> and TSP were in the ranges 2.2-9.6 and 2.0-9.0,
- 408 respectively.
- 409 *3.3.2. PM*<sub>10</sub> *chemical composition*
- 410 3.3.2.1. Carbonaceous content
- On average, the indoor concentration of the total carbonaceous content (TC = OC + EC) was
- 4.7 times higher during the occupancy than non-occupancy periods (Fig. 4A). OC was the most
- abundant carbonaceous component, reaching  $26.6 \pm 11.8$ ,  $5.63 \pm 0.89$  and  $8.21 \pm 3.09$  µg m<sup>-3</sup>
- 414 for occupancy, non-occupancy periods and outdoor samples, respectively. Unlike outdoors, a
- strong correlation was found between indoor  $PM_{10}$  and OC concentrations ( $R^2 = 0.99$ ) (Fig. 4C
- and 4D). The I/O ratio of OC, during working hours, ranged between 1.8 and 9.7 with a mean
- value of 4.0. I/O >1 and a good relationship between indoor PM<sub>10</sub> and OC concentrations
- 418 pointed out to the existence of indoor sources of organic compounds. The products used for
- 419 hair treatments and biological matter, such as filings of nails and hard nail gels, tiny hair snippet
- and epidermis, can also contribute to OC-bound coarse PM (Rogula-Kopiec et al., 2017). Indoor
- and outdoor EC concentrations, during the occupancy period, were substantially lower (3.80  $\pm$
- 422 1.39 and  $4.30 \pm 1.63 \,\mu g \, m^{-3}$ , respectively) and presented a mean I/O ratio of 0.9. Elemental
- carbon is mostly emitted from combustion processes or pyrolysis of biological material (Jones
- 424 and Harrison, 2005).
- Total carbon accounted for  $34.1 \pm 2.2$ ,  $28.7 \pm 1.0$  and  $25.0 \pm 5.2$  % wt. of PM<sub>10</sub> during occupancy
- and non-occupancy periods and outdoor samples, respectively, with an OC/EC ratio between
- 427 1.5-7.8 (Fig. 4B). OC constituted the major mass fraction, accounting for 29.5  $\pm$  1.8 and 16.2  $\pm$
- 4.5 % wt. of PM<sub>10</sub> in indoor and outdoor samples during working hours, respectively, while the
- 429 corresponding EC fractions were substantially lower  $(4.53 \pm 1.42 \text{ and } 8.86 \pm 3.51 \text{ wt. of PM}_{10},$
- respectively). Mass contributions to total carbon of indoor OC and EC during occupancy and
- night-time periods were practically the same, around 87% and 13%, respectively. Outdoor OC

and EC accounted for 65% and 35% of TC, respectively. The increase of mass shares of EC in

outdoor samples suggested road traffic contribution to ambient PM. Similar to the present study,

Rogula-Kopiec et al. (2017) provided strong evidence of the contribution of indoor sources of

OC to PM-bound carbon in beauty salons. The authors recorded a mass contribution of OC to

total carbon in PM<sub>4</sub> between 94 and 97% for indoor samples; their mean I/O ratios of PM<sub>4</sub>-

bounded OC and EC were in the ranges 2.6 - 12.0 and 1.4 - 3.7, respectively.

438 *3.3.2.2. Trace elements and water-soluble ions* 

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In order to achieve a chemical mass closure, measured element concentrations were converted to their common oxides, which constituted around 10.7, 44.3 and 40.6 % wt. of the total PM<sub>10</sub> mass in samples collected indoors during the occupancy and non-occupancy periods and outdoors, respectively (Fig. 5A). Among them, Na, Mg, Al, Si, S, K, Ca and Fe were the most abundant elements (Table S5). An appreciable decrease of indoor concentrations was registered for all elements during non-occupancy periods, which can be related to dust settling due to the absence of human activity at night. I/O ratios higher than one were observed for Cu (2.8), Ni (2.4), Br (2.2) and Mo (1.8), suggesting the presence of indoor sources. Inside beauty salons, emissions of these elements can be associated with the use of hair cosmetics. Some metals (Cd, Pb, Cr, Cu, Co, Ni, Mn and Fe) have been detected in several hair treatment products, including hair relaxers, pomades, dyes, conditioners and shampoos (Borowska and Brzóska, 2015; Iwegbue et al., 2016). In this study indoor concentrations, observed for Cu (99.2  $\pm$  39.4 ng m<sup>-</sup> <sup>3</sup>), were still significantly higher. Lower indoor concentrations of Cu ( $48.2 \pm 46.8$  ng m<sup>-3</sup>) were measured in beauty chops of Kwang-Ju (South Korea) (Son et al., 2006). Copper was found in shampoos and hair care products with concentrations ranging from 0.07 to 12.80 µg g<sup>-1</sup>, respectively (Amartey et al., 2011; Iwegbue et al., 2016; Lavilla 2009; Ullah et al., 2017). The international use of some elements (Ni, Sb, As, Cd, Cr and Co) as ingredients of cosmetic products is prohibited by Annex II of Directive 76/768/EEC of the European Union due to their high toxicity (Bocca et al., 2014). Nevertheless, these compounds persist in existing cosmetic products, owing to their ubiquitous nature and contamination from production processes. A wide concentration range of Ni, up to  $11.3 \pm 10.5 \,\mu g \, g^{-1}$ , was found in anti-dandruff hair shampoos and other hair care products (Amartey et al., 2011; Arshad et al., 2020; Iwegbue et al., 2016; Lavilla et al., 2009; Ullah et al., 2017). In the present study, Ni, Pb, As and Cr presented relatively low levels in all samples (Table S5). Significantly higher mean concentrations of Ni  $(83.9 \pm 212.2 \text{ ng m}^{-3})$ , Pb  $(70.2 \pm 31.8 \text{ ng m}^{-3})$ , Cr  $(299 \pm 110 \text{ ng m}^{-3})$ , Zn  $(370 \pm 751 \text{ ng m}^{-3})$  and Mg  $(259 \pm 209 \text{ ng m}^{-3})$  inside of beauty shops located near roadways compared to outdoor air were measured by Son et al. (2006). In their study, the I/O ratios of metals were generally lower than one, indicating contribution of vehicle emissions to poor indoor air quality. Bromine is one of the most used chemicals in the production of flame retardants (BFRs), which are added to plastics and applied in a series of commercial products and construction materials to meet fire safety standards. Additive BFRs do not form a chemical bond with the material and can be easily released (through abrasion, volatilisation, and leaching during usage) into the indoor air, where they are partitioned between the dust/particulate and gas phases (Genisoglu et al., 2019). In the present study, indoor sources of Br may be related to the use of hairdressing tools and electrical equipment (e.g. hairdryer, hot air stylers, curling tongs, hair straighteners, clipper accessories, etc). In this study, enrichment factors (EF) were calculated for each element to show the degree of enrichment of a given element compared to the relative abundance of that element in crustal material. EF is defined as EF =  $(E/R)_{air}/(E/R)_{crust}$ , where E and R refer to concentrations of element E under analysis and a reference element R. Fe was used as reference element and the average element concentrations in the upper continental crust were taken from Wedepohl (1995). According to Table S5, Se exhibited the highest EFs (564) in outdoor samples. Br, Cu, As, Mo, Zn, S, Cl and Pb showed moderate enrichment (9 < EF < 66). A high enrichment suggests predominance of anthropogenic sources for these elements and points out that a variety of emissions may contribute to their loading in the ambient air. On the contrary, low enrichment factors (< 5) were observed for Na, Mg, Al, Si, P, K, Ca, Ti, V, Cr, Mn, Rb, Sr and Y, indicating negligible contribution of anthropogenic sources and a main origin in the airborne dust. Water-soluble ions accounted for  $2.52 \pm 0.21$  (indoor, occupancy),  $12.40 \pm 1.10$  (indoor, nonoccupancy),  $10.30 \pm 0.96$  (indoor, weekend) and  $7.93 \pm 0.91$  (outdoor, occupancy) %wt. of  $PM_{10}$ . Mean I/O ratios of  $SO_4^{2-}$  and  $Na^+$  were > 1, whereas the ratios were < 1 for all other constituents (Fig. 6). The indoor concentrations of Ca<sup>2+</sup>, NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> measured during the occupancy periods were 3.9, 3.5 and 2.7 times lower than the corresponding outdoor levels, respectively. Among cations, Ca<sup>2+</sup> and NH<sub>4</sub><sup>+</sup> were dominant in outdoor samples collected during working hours, while Ca<sup>2+</sup> and K<sup>+</sup> were the major ions in the corresponding indoor samples. The most abundant anions were NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> in all samples. Ionic balances have been commonly used to shed light on the aerosol acidity and to determine any possible missing ionic species (Tripathee et al., 2016; Wang et al., 2006). In the present study, a cation excess was observed. The anion deficit may be due to carbonate, which has not been measured in this study.

498 *3.3.2.3. Organic matter* 

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To account for the mass of unmeasured hydrogen, oxygen and other atoms in organic matter 499 (OM) of PM<sub>10</sub>, the OM concentration was obtained by multiplying the OC concentration by a 500 factor of 1.8 (Polidori et al., 2008). In the present study, OM accounted for 53.2, 45.2 and 29.1 501 % wt. of PM<sub>10</sub> in indoor samples collected during occupancy, non-occupancy periods and 502 outdoors, respectively (Fig. 5A). Multiple compounds were found in the PM<sub>10</sub> organic extracts. 503 Concentrations of major identified compounds are presented in Table 2, while their complete 504 list is given in the Supporting Information (Table S6). Aliphatic alcohols and fatty acids were 505 506 the major compound classes, followed by phthalates, glycerol derivatives, alkyl esters of fatty 507 acids and phenolic compounds (Fig. 5B and 5C). Other compound classes represented a minor 508 contribution to  $PM_{10}$ . 509 Highly variable levels of aliphatic alcohols (C<sub>8</sub> to C<sub>26</sub>) were detected in PM<sub>10</sub> samples (Table 2 and Table S6). Long-chain alcohols, as well as fatty acids, are commonly present in 510 511 atmospheric aerosol and can derive from both natural (e.g. vascular plant waxes, microbiota) and anthropogenic sources (e.g. fossil fuel combustion, biomass burning, cooking activities, 512 513 etc). In this study, on average, total concentrations of alcohols were as follows:  $7614 \pm 7298$  ng m<sup>-3</sup> (indoor, working hours), 489 ng m<sup>-3</sup> (indoor, night), 332 ng m<sup>-3</sup> (indoor, weekend, daytime) 514 and  $88.8 \pm 30.4$  ng m<sup>-3</sup> (outdoor, working hours). The highest indoor concentrations during 515 working hours were recorded for 1-octadecanol, 1-hexadecanol and 1-tetradecanol. I/O ratios 516 517 of these alcohols ranged from 30 to 338. Their indoor concentrations were from 3 to 45 times higher during occupancy than non-occupancy periods, suggesting the presence of strong indoor 518 sources. Cetyl and stearyl alcohols are added as non-ionic surfactants to shampoo and hair 519 conditioners to reduce the static electricity generating effects caused by the anionic surfactants 520 521 (Dias, 2015). Furthermore, aliphatic alcohols are extensively used in consumer, cleaning and personal care products such as laundry powder, general/hard surface cleaners, fabric 522 conditioners, styling gels and mousses, cleaners, body washes, skin lotions and creams 523 (Veenstra et al., 2009). 524 Highly variable levels of alkanoic acids from C<sub>8</sub> to C<sub>26</sub> and some alkenoic acids were also 525 526 detected in organic extracts (Table 2 and Table S6). On average, total concentrations of carboxylic acids, measured inside the beauty salon, were  $5262 \pm 2744$  ng m<sup>-3</sup> and 375 ng m<sup>-3</sup> 527 528 during working hours and at night-time, respectively, and far exceeded those observed outside. The professional activities inside the beauty salon and the use of various hair products can 529 530 explain the very high I/O ratios (up to 194) of some acids. Myristic acid was the most abundant indoors, followed by palmitic, palmitoleic, pentadecanoic and linoleic acids. Fatty acids are 531 532 commonly present in vegetable oils such as coconut, palm, almond, grape seed, olive, corn,

sesame, wheat germ, among others, which are widely used in hair cosmetics (Agarwal et al., 2018; Briefs and Digne, 2016; Mank and Polonska, 2016). The most common fatty acids in vegetable oils are saturated palmitic and stearic acids, monounsaturated oleic acid and polyunsaturated linoleic acid (Veenstra et al., 2009). Relatively high levels of C<sub>14</sub>-C<sub>16</sub>, C<sub>18</sub> and C<sub>19</sub> acids, observed in outdoor samples, can derive from anthropogenic sources such as coal and biomass burning, vehicular exhaust emissions and cooking activities (Harvey et al 2012; Rogge et al 1993; Zhao et al 2007). Significant amounts of alkyl fatty acid esters were found in PM<sub>10</sub> (Fig. 5B). Most of them presented higher indoor concentrations ( $\Sigma_{21} = 546 \pm 252$  ng m<sup>-3</sup>) than outside ( $\Sigma_{21} = 20.6 \pm 14.2$ ng m<sup>-3</sup>) the beauty salon (working hours), pointing out the impact of indoor sources. Among 543 them, alkyl esters of decanedioic, hexadecenoic and octanoic acids were the most abundant (Table 2). Alkyl esters, such as ethyl myristate, ethyl palmitate, ethyl stearate and ethyl oleate, are found in many hair products (Hartwig et al., 2003). Ethyl-hexyl palmitate, isopropyl myristate and isopropyl palmitate can be found at high concentrations in cosmetics. Moreover, alkyl esters, also used in cosmetic sprays at high concentrations (77% isopropyl myristate in hair sprays, 45% ethylhexyl palmitate in indoor tanning preparations, and 23% isopropyl myristate in deodorant formulations), could possibly be inhaled when aerosolised. The synthetic wax, widely used in cosmetic and personal care applications, is composed of a mixture of esters of saturated fatty acids and fatty alcohols with carbon chain lengths between 14:0 and 18:1 (Fiume et al., 2015). Phthalate esters are ubiquitous environmental contaminants and predominantly used as plasticisers to improve the flexibility of polymers in a variety of consumer products, commodities and building materials. They are not chemically bound to plastic polymers and can leach, migrate or evaporate into the air (Heudorf et al., 2007). With regard to cosmetics, phthalates were detected in many formulations, including perfumes, nail polish, hair products and deodorants (Hyun and Byung, 2004). In this study, on average, the total indoor 558 concentration of plasticisers were significantly higher (595  $\pm$  507 ng m<sup>-3</sup>) than those measured in background air at night-time (198 ng m<sup>-3</sup>) and on the weekend (346 ng m<sup>-3</sup>). Among the identified phthalates, bis(2-ethylhexyl)phthalate also known as DEHP was the most abundant (Table 2). DEHP is the most common plasticiser of polymer products, mainly in flexible polyvinyl chloride (PVC) used in numerous consumer products. Relatively high concentration of DEHP observed inside the salon are probably related to the emissions from building materials, such as flooring, cables, profiles, etc. DEHP is considered as being carcinogenic by exposure via inhalation and brings concerns in indoor and occupational environments (Miao et

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al., 2017). Regarding hairdressing salons, only a few studies have reported concentrations of 567 phthalate esters. Chang et al. (2018) studied air quality in working, washing, technical and 568 reception areas in hair salons and recorded concentrations of dibutyl phthalate (DBP), diethyl 569 phthalate (DEP), dimethyl phthalate (DMP), butyl benzyl phthalate (BBP) and DEHP between 570  $3.09 \times 10^{-2}$  and 4.96 µg m<sup>-3</sup>. Ronda et al. (2009) evaluated the exposure of chemical compounds 571 in the air of Spanish hairdresser salons and reported DEP concentrations (mean, minimum and 572 maximum) of 0.48 (0.01-0.97) and 0.12 (0.00-0.75) mg m<sup>-3</sup> for personal and stationary samples, 573 respectively. Labrèche et al. (2003) reported mean concentrations of 0.003 mg m<sup>-3</sup> for DBP 574 575 measured inside hair salons in Quebec. Similarly, the mean total indoor concentrations of *phenolic compounds* (307  $\pm$  307 ng m<sup>-3</sup>) 576 measured during the occupancy period largely exceeded their night-time (50.1 ng m<sup>-3</sup>) and 577 outdoor (27.4  $\pm$  26.5 ng m<sup>-3</sup>) counterparts (Fig. 5C). Some of the identified phenolics (Table 2-578 3) are extensively used as natural or synthetic antioxidants in rubber, plastic, cosmetic and 579 pharmaceutical industries to retard the oxidation process (Liu and Mabury, 2019; Soto et al., 580 2015). 581 582 *n-Alkanes* in the range from C<sub>11</sub> to C<sub>35</sub> were quantified in this study (Table S6). The mean total concentrations of *n*-alkanes were  $145 \pm 104$ , 1.36 and  $7.57 \pm 5.44$  and  $ng m^{-3}$  in samples 583 584 collected in the salon during working hours, non-working hours and outdoors, respectively. The 585 highest average indoor concentrations, during working hours, were registered for C24, C23 and C<sub>25</sub>. Extremely high I/O ratios of 144, 111, 47.6 and 46.7 were found for C<sub>25</sub>, C<sub>24</sub>, C<sub>27</sub> and C<sub>23</sub>, 586 respectively (Table 2). Straight-chain saturated hydrocarbons are a part of mineral oils and 587 waxes, which are incorporated as moisturisers and non-allergenic ingredients in many cosmetic 588 products (skin creams, lotions, sunscreens, lip care products and hair gels). Concentrations of 589 590 mineral oils in cosmetics can range from 1% to 99% depending on the product (Chuberre et al., 2019). Significantly lower I/O (0.09-1.04) ratios and very low concentrations of alkenes ( $C_{12}$ , 591 592  $C_{14}$ ,  $C_{16}$ ,  $C_{18}$  and  $C_{21}$ ) were observed. Contrary to homologous series of fatty alkanes, alcohols and acids, saccharides and polyols 593 594 presented low I/O ratios, which suggest the predominance of outdoor sources (Table 2). Among 595 saccharides, levoglucosan was the most abundant compound. Levoglucosan is well recognised as a tracer of biomass burning, which is formed from the pyrolysis of cellulose and 596 hemicellulose (Bhattarai et al., 2019; Leithead et al., 2006). Similarly, I/O ratios for most of 597 PAHs were less than one, ranging from 0.04 to 0.60, except for acenaphthene and fluorene 598 (Table S6). PAHs are by-products of incomplete combustion of fossil fuels and biomass. 599

- 600 Many other organic oxygenated compounds, which are constituents of various consumer
- products, were detected in the indoor air of the beauty salon (Table 2 and Table 3). Many of
- them presented very high mean I/O ratios or weren't even detected in outdoor PM<sub>10</sub> samples,
- 603 indicating strong indoor emissions. The use of specific cosmetic applications and cleaning
- products, and professional activities can contribute to pollutant build-up in beauty salons.
- 605 *3.4 Health risk assessment*
- The carcinogenic (excess cancer risk (CR)) and non-carcinogenic risks (hazard quotients (HR)),
- associated with inhalation exposure by hairdressers to VOCs and PM<sub>10</sub>-bound metals, PAHs
- and trace elements are presented in Tables S7 and S8 (supporting information). Formaldehyde
- presented a cancer risk between  $1 \times 10^{-4}$  and  $1 \times 10^{-6}$  suggesting a "possible risk". CR and HQ
- of other studied compounds were lower than the USEPA guidelines and thus can be interpreted
- as being risk-free. It should be noted that these results are only indicative and non-conclusive
- due to the short time series. However, endocrine disrupting chemicals, such as phthalates (Li et
- al., 2021; Piazza and Urbanetz, 2019), were found at high concentrations in this study, which
- may require special attention in future studies.
- 615 *3.5. Study strengths and limitations*
- Although exploratory, this is a pioneer study in detailed PM<sub>10</sub> chemical characterisation in
- beauty salons. More than 200 organic compounds, as well as the carbonaceous content, trace
- 618 elements and water-soluble ions were quantified in indoor and outdoor samples, during
- occupancy (working hours) and non-occupancy (night-time) periods. Additionally, VOCs and
- 620 comfort parameters were monitored.
- However, some limitations might be pointed out. Measurements were carried out within one
- week only in wintertime and may not reflect seasonal differences of natural ventilation.
- Regarding PM<sub>10</sub> measured by gravimetry, two samples were collected inside (occupancy and
- non-occupancy periods) and one outside (occupancy period only) of the salon for each sampling
- day. Accordingly, each indoor sample was compared with the respective outdoor sample. VOCs
- and carbonyls were only measured inside the beauty salon, which does not allow to trace their
- origin (e.g. traffic or internal emissions). To get around this difficulty, VOC and carbonyl levels
- measured in the vicinity in another monitoring campaign in the same season were taken for
- 629 comparative purposes. Only a long-term sampling campaign with detailed analysis of the
- 630 chemical composition would allow the application of source apportionment methodologies,
- such as positive matrix factorisation. The quantities of products used were not monitored, which
- makes it difficult to interpret the concentrations obtained.

It should also be borne in mind that the levels of both BTEX and PM measured inside the salon do not reflect emissions only from the use of cosmetic products. Many compounds can come from skin and clothing of customers, as well as be emitted from building materials and furnishings. In addition, traffic emissions can infiltrate and accumulate, contributing to indoor concentrations of both BTEX and PM. In conclusion, further studies to address the aforesaid limitations are highly recommended. Given that hairdressers are exposed to high concentrations of pollutants with a potentially dangerous composition, it would be desirable to assess toxicity, through bioassays, especially of particulate matter.

#### 4. Conclusions

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The results of this study, based on a weeklong sampling campaign inside and outside a beauty salon (León, Spain), allowed, for the first time, to characterise the chemical composition of PM<sub>10</sub> in this type of professional environment. PM<sub>10</sub> indoor concentrations exceeded the 24-h guideline of 50  $\mu g\ m^{-3}$  recommended by the WHO. From gravimetric measurements, average PM<sub>10</sub> concentrations of 89  $\pm$  39 and 50  $\pm$  12  $\mu g$  m<sup>-3</sup> were recorded in the salon during the occupancy period and in the outdoor air, respectively. I/O ratios of PM<sub>10</sub>, as well as of the majority of PM<sub>10</sub>-bound organic compounds, were higher than one and in some cases as high as 100, thus indicating strong emissions from indoor sources. OC constituted the major mass fraction of PM<sub>10</sub> during occupancy periods, accounting for 29.5  $\pm$  1.8 and 16.2  $\pm$  4.5 wt%. in indoor and outdoor samples, respectively. More than 200 individual organic oxygenated compounds were detected in PM<sub>10</sub>, aliphatic alcohols and fatty acids being the most abundant, followed by phthalates, glycerol derivatives, alkyl esters of fatty acids and phenolic compounds. Many of the identified compounds are extensively used in hair cosmetics, cleaning and personal care products, which can be the source of indoor emissions. It is worth noting that, in this study, metals and PAHs presented I/O<1 and significantly lower levels, when compared to other PM<sub>10</sub>-bound species. Simultaneously, comfort parameters, concentrations of BTEX, formaldehyde and acetaldehyde were assessed. CO<sub>2</sub> concentrations were correlated with the number of clients attending the salon. The air exchange rate values indicated lack of adequate ventilation. BTEX, formaldehyde and acetaldehyde were found in concentrations below the recommended guidelines. Formaldehyde presented a higher cancer risk  $(4.6 \times 10^{-6})$  than the USEPA guideline level  $(1 \times 10^{-6})$ 10<sup>-6</sup>), suggesting a "possible risk". The total estimated excess cancer risk of exposure to multiple compounds was  $9.3 \times 10^{-6}$ , which is lower than the USEPA acceptable risk, but not negligible.

Although exploratory, this study can be considered as an evaluation of the "worst case scenario". As concentrations are generally higher in winter due to lower ventilation rates, the adoption of measures to improve air quality must comply with the precautionary principle

aimed at preventing the worst possible consequences.

In conclusion, professional activities inside a beauty salon and the use of various hair and cosmetic products can greatly contribute to high indoor levels of organic air pollutants. The installation of heating and ventilation systems should be contemplated to maintain thermal comfort parameters and reduce indoor pollutant concentrations. In addition, to improve air quality in beauty salons, air quality guidelines or a mandatory occupational regulatory framework is needed. Finally, identifying and prohibiting cosmetic products with potentially toxic emissions could reduce pollutant exposures of both workers and clients.

### Acknowledgments

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678 The sampling campaign was partially supported by the Spanish Ministry of Economy and Competitiveness (Grant TEC2014-57821-R), the University of León (Programa Propio 679 680 2015/00054/001 and 2018/00203/001) and the AERORAIN project (Ministry of Economy and Competitiveness, Grant CGL2014-52556-R, co-financed with European FEDER funds). Other 681 part of the monitoring campaign and the analytical determinations of this work were funded by 682 the project "Chemical and toxicological SOurce PROfiling of particulate matter in urban air 683 (SOPRO)", POCI-01-0145-FEDER-029574, supported by FEDER, through COMPETE2020 -684 Programa Operacional Competitividade e Internacionalização (POCI), and by national funds 685 (OE), through FCT/MCTES. An acknowledgment is due to the Portuguese Foundation of 686 Science and Technology (FCT) and to the POHP/FSE funding programme for the fellowships 687 with the references SFRH/BD/117993/2016 and SFRH/BPD/123176/2016. Ana Vicente is 688 subsidised by national funds (OE), through FCT, I.P., in the framework contract foreseen in the 689 numbers 4, 5 and 6 of article 23, of the Decree-Law 57/2016, of August 29, changed by Law 690 57/2017, of July 19. Thanks are due, for the financial support to CESAM 691 (UIDB/50017/2020+UIDP/50017/2020), to FCT/MEC through national funds, and the co-692 693 funding by the FEDER, within the PT2020 Partnership Agreement and Compete 2020. F. Oduber and C. Blanco-Alegre acknowledge the grants BES-2015-074473 and FPU16-05764 694 695 from the Spanish Ministry of Economy and Competitiveness and from the Ministry of 696 Education, Culture and Sports, Spain, respectively.

#### **Conflicts of interest**

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698 The authors declare no conflict of interest.

# **Appendix A. Supporting Information**

- Supporting information to this article can be found online at https://doi. org/XXX
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Table 1. Comparison of BTEX indoor concentrations (mean  $\pm$  SD, (min-max),  $\mu g$  m<sup>-3</sup>) of the present study with those reported in the literature.

| Study/                 | Location                           | D                                 | Toluono                            | Ed. 11                              | / <b>V</b> 1                     | - V-lana                            |  |
|------------------------|------------------------------------|-----------------------------------|------------------------------------|-------------------------------------|----------------------------------|-------------------------------------|--|
| Limit values           | N of salons                        | Benzene Toluene                   |                                    | Ethylbenzene                        | <i>m/p</i> -Xylene               | o-Xylene                            |  |
| STEL/TWA <sup>a</sup>  | -                                  | 3.25/-                            | 192/384                            | 441/484                             | 221/442                          | 221/442                             |  |
| $(mg m^{-3})$          |                                    |                                   |                                    |                                     |                                  |                                     |  |
| This study             | León, Spain, 1 beauty salon        | $1.6 \pm 0.3  (1.3 \text{-} 2.1)$ | $4.6 \pm 1.3 \ (3.2 \text{-} 6.6)$ | $1.55 \pm 0.3 \ (1.3 \text{-} 2.2)$ | $3.5 \pm 1.1 (2.6 - 6.3)$        | $1.65 \pm 0.4 \ (1.3 \text{-} 2.6)$ |  |
| Lamplugh et al. (2019) | Colorado, USA, 6 nail salons       | (3.13-51.8)                       | (26.7-816)                         | (1.65 - 9.52)                       | 5.16                             | - 34.6 <sup>b</sup>                 |  |
| Moradi et. al. (2019)  | Tehran, Iran, 36 beauty salons     | 4.9                               | 118.7                              | 7.5                                 | 16.7                             | 7.5                                 |  |
| Baghani et al. (2018)  | Ardabil, Iran, 50 beauty salons    | $32.4 \pm 26.4$                   | $16.1 \pm 14.3$                    | $62.4 \pm 32.4$                     | $13.8 \pm 11.6^{b}$              |                                     |  |
| Hadei et al. (2018)    | Tehran, Iran, 20 beauty salons     | (~5-10)                           | (~5-12)                            | (~8-22)                             | (~10                             | 0-23) <sup>b</sup>                  |  |
| Tsigonia et al. (2010) | Athens, Greece, 4 beauty salons    | -                                 | 3-67°                              | -                                   | (0-                              | 10) <sup>b</sup>                    |  |
| Ronda et al. (2009)    | Alicante, Spain, 10 hairdressing   | $0.01\times10^3$                  | $0.12\times10^3$                   | $0.01\times10^3$                    | $0.03\times10^3$                 | $0.01\times10^3$                    |  |
|                        | salons                             | $(0.00\text{-}0.02) \times 10^3$  | $(0.02\text{-}0.31) \times 10^3$   | $(0.00 \text{-} 0.04) \times 10^3$  | $(0.00\text{-}0.03) \times 10^3$ | $(0.00\text{-}0.03) \times 10^3$    |  |
| Bruno et al. (2008)    | Italy, Bari, 2 hairdressing salons | 2.6-2.8                           | 20.7-55.2                          | 5.5-10.6                            | 51.6-102.4                       | 18.1-30.4                           |  |
| Son et al. (2006)      | Kwang-Ju, S. Korea                 | $0.2 \pm 0.7$                     | $9.8 \pm 5.8$                      | $0.6 \pm 1.8$                       | $30.3\pm20.3^{b}$                |                                     |  |
|                        | 20 beauty shops                    | -                                 | -                                  | -                                   | -                                | -                                   |  |
| Labrèche et al. (2003) | Montreal, Canada,                  | -                                 | $0.54\times10^3$                   | -                                   | -                                | -                                   |  |
|                        | 26 hairdressing salons             |                                   | $(0.02-8.37) \times 10^3$          |                                     |                                  |                                     |  |

<sup>&</sup>lt;sup>a</sup>STEL = Threshold Limit Value (Spain); TWA = Time Weighted Average is a TLV based on a 8-hour workday and a 40-hour workweek from INSHT (2014); <sup>b</sup>m,p-xylene + o-xylene.

<sup>&</sup>lt;sup>c</sup>8-h-TWA levels.

Table 2. Concentrations (ng  $\mbox{m}^{-3}\mbox{)}$  of major oxygenated organic compounds in  $PM_{10}.$ 

|   | T., 1            | T. 1        | T., 1             | 0.41                                   | I/O      |
|---|------------------|-------------|-------------------|--|----------|
|   | Indoor           | Indoor non- | Indoor<br>weekend | Outdoor                                | I/O      |
| Alkanes   | occupancy        | occupancy   | weekend           | occupancy                              | occupanc |
| Tricosane                                       | $24.6 \pm 14.9$  | bdl         | 1.50              | $0.526 \pm 1.11$                       | 47       |
| Tetracosane                                     | $30.9 \pm 21.3$  | bdl         | bdl               | $0.279 \pm 0.623$                      | 111      |
| Pentacosane                                     | $23.9 \pm 19.9$  | bdl         | bdl               | $0.279 \pm 0.023$<br>$0.166 \pm 0.371$ | 144      |
| Hexacosane                                      | $14.1 \pm 13.7$  | bdl         | bdl               | bdl                                    | -        |
| Heptacosane                                     | $9.81 \pm 9.25$  | bdl         | bdl               | $0.206 \pm 0.461$                      | 48       |
| Aliphatic alcohols                              | 7.01 ± 7.23      | oui         | our               | 0.200 ± 0.101                          | 10       |
| 1-Dodecanol                                     | $11.4 \pm 6.7$   | 10.3        | 6.94              | $0.906 \pm 0.547$                      | 13       |
| 1-Tetradecanol                                  | $192 \pm 275$    | 70.9        | 87.2              | $6.37 \pm 2.28$                        | 30       |
| 1-Pentadecanol                                  | $34.3 \pm 18.7$  | 28.6        | 16.6              | $10.4 \pm 4.27$                        | 3.3      |
| Hexadecanol                                     | $2502 \pm 2413$  | 247         | 147               | $18.1 \pm 5.25$                        | 138      |
| 1-Octadecanol (Stearyl alcohol)                 | $4689 \pm 4844$  | 103         | 54.6              | $13.9 \pm 5.05$                        | 338      |
| 1-Nonadecanol                                   | $10.8 \pm 11.0$  | 0.303       | 0.242             | $1.30 \pm 2.00$                        | 8.4      |
| 1-Eicosanol                                     | $91.8 \pm 92.8$  | 0.978       | bdl <sup>b</sup>  | $0.965 \pm 0.890$                      | 95       |
| 1-Heneicosanol                                  | $2.37 \pm 2.57$  | nd          | nd                | $0.095 \pm 0.116$                      | 25       |
| 1-Docosanol (Behenyl alcohol)                   | $17.5 \pm 20.4$  | 0.462       | 0.460             | $0.912 \pm 1.04$                       | 19       |
| Aliphatic carboxylic acids                      |                  | *****       |                   | ***                                    | -,       |
| 1-Decanoic (caproic) acid                       | $17.2 \pm 15.3$  | 1.07        | 3.99              | $0.849 \pm 0.518$                      | 20       |
| 1-Dodecanoic (lauric) acid                      | $25.4 \pm 9.1$   | 18.2        | 65.7              | $4.66 \pm 1.94$                        | 5.5      |
| 1-Tridecanoic acid                              | $3.24 \pm 3.68$  | 5.59        | 5.85              | $0.548 \pm 0.591$                      | 5.9      |
| C <sub>13</sub> acid isomers                    | $11.4 \pm 12.1$  | nd          | nd                | $1.21 \pm 1.52$                        | 9.4      |
| 1-Tetradecanoic (myristic) acid                 | $1274 \pm 543$   | 274         | 141               | $26.9 \pm 9.7$                         | 47       |
| Tetradecenoic acid                              | $52.9 \pm 40.8$  | 1.49        | 2.96              | nd                                     | -        |
| 1-Pentadecanoic acid                            | $526 \pm 295$    | 22.3        | 25.7              | $4.27 \pm 2.05$                        | 123      |
| Pentadecenoic acid                              | $46.5 \pm 50.7$  | nd          | nd                | nd                                     | -        |
| C <sub>15</sub> acid isomers                    | $153 \pm 143$    | 12.5        | 9.78              | nd                                     | _        |
| 1-Hexadecanoic (palmitic) acid                  | $950 \pm 594$    | 0.067       | 206               | $47.7 \pm 35.1$                        | 20       |
| C <sub>16</sub> acid isomers                    | $294 \pm 218$    | 8.20        | 4.34              | nd                                     | -        |
| 9-cis-Hexadecenoic (palmitoleic)                | 27. = 210        | 0.20        |                   | 110                                    |          |
| acid  | $600 \pm 414$    | 0.033       | 0.544             | $3.09 \pm 5.59$                        | 194      |
| 1-Heptadecanoic acid                            | $145 \pm 94$     | 0.046       | 7.19              | $1.89 \pm 1.29$                        | 77       |
| C <sub>17</sub> acid isomers                    | $217 \pm 139$    | 4.57        | 11.1              | $6.48 \pm 5.89$                        | 34       |
| Heptadecenoic acid                              | $105 \pm 97$     | nd          | nd                | nd                                     | -        |
| 1-Octadecanoic (stearic) acid                   | $210 \pm 116$    | 0.192       | 42.6              | $62.2 \pm 55.7$                        | 3.4      |
| cis,cis-9,12-Octadecadienoic                    | 210 = 110        | 0.172       | .2.0              | 02.2 = 00.7                            |          |
| (linoleic) acid                                 | $56.0 \pm 58.8$  | 0.138       | 0.896             | $1.73 \pm 2.18$                        | 32       |
| cis-9-Octadecenoic (oleic) acid                 | $380 \pm 260$    | bdl         | 5.21              | $5.85 \pm 5.01$                        | 65       |
| cis-11-Octadecenoic acid                        | $20.1 \pm 25.4$  | nd          | nd                | nd                                     | -        |
| 1-Nonadecanoic acid                             | $9.72 \pm 7.03$  | 0.021       | Nd                | $0.243 \pm 0.198$                      | 40       |
| 1-Eicosanoic (arachidic) acid                   | $19.3 \pm 10.2$  | 0.264       | 1.31              | $3.08 \pm 2.70$                        | 6.3      |
| Eicosenoic acid                                 | $9.26 \pm 8.10$  | nd          | nd                | nd                                     | -        |
| 1-Docosanoic (behenic) acid                     | $10.8 \pm 5.0$   | 1.63        | 1.68              | $4.75 \pm 3.66$                        | 2.3      |
| 1-Tetracosanoic acid                            | $19.7 \pm 6.79$  | 3.54        | nd                | $6.35 \pm 2.80$                        | 3.1      |
| 1-Pentacosanoic acid                            | $5.28 \pm 2.84$  | nd          | nd                | $0.318 \pm 0.636$                      | 17       |
| Alkyl esters of fatty acids                     | 0.20 = 2.0 .     | 114         | 110               | 0.010 = 0.000                          | -,       |
| Isopropyl myristate                             | $24.4 \pm 26.3$  | 57.9        | nd                | $3.75 \pm 5.57$                        | 6.5      |
| Methyl palmitate                                | $6.98 \pm 8.04$  | 3.02        | 81.6              | $6.46 \pm 4.10$                        | 1.1      |
| Isopropyl palmitate                             | $8.42 \pm 12.00$ | nd          | 25.1              | $0.845 \pm 0.979$                      | 10       |
| 2-Hydroxyethyl palmitate                        | $11.4 \pm 11.5$  | nd          | nd                | nd                                     | -        |
| 1-Monomyristin                                  | $39.1 \pm 30.9$  | nd          | 1.55              | nd                                     | _        |
| Palmitic acid methyl ester                      | $48.2 \pm 38.6$  | 160         | 121               | $3.31 \pm 2.11$                        | 15       |
| I annitic acid methyl ester Isopropyl palmitate | $56.6 \pm 55.5$  | 57.3        | 22.2              | $0.519 \pm 0.453$                      | 109      |
| 1-Propylpentyl laurate                          | $9.61 \pm 10.39$ | 12.7        | 9.68              | $0.519 \pm 0.433$<br>$0.505 \pm 0.419$ | 109      |
| Methyl stearate                                 | $26.7 \pm 32.2$  | 56          | 12.3              | $0.702 \pm 0.534$                      | 38       |
| Dodecyl octanoate                               | $4.80 \pm 5.46$  | 3.02        | nd                | $0.702 \pm 0.334$<br>$0.126 \pm 0.183$ | 38       |
| Tetradecyl octanoate                            | $7.73 \pm 11.03$ | nd          | nd                | nd                                     | -        |
| Hexadecyl octanoate                             | $24.5 \pm 32.1$  | nd          | nd                | nd                                     | _        |

| **                                 | <b>70.7. 10.0</b> | 44.0         | 21.2  | 104 100           | 2.5 |
|------------------------------------|-------------------|--------------|-------|-------------------|-----|
| Hexadecyl 2-ethylexanoate          | $50.5 \pm 42.8$   | 11.8         | 21.3  | $1.86 \pm 1.29$   | 27  |
| Octadecyl 2-ethylexanoate          | $31.5 \pm 30.0$   | 2.76         | nd    | $0.147 \pm 0.294$ | 214 |
| Dioctyl sebacate                   | $164 \pm 285$     | nd           | nd    | nd                | -   |
| Hexadecyl palmitate                | $18.5 \pm 21.1$   | nd           | nd    | $0.270 \pm 0.390$ | 69  |
| Dibutyl adipate                    | $5.75 \pm 8.87$   | nd           | 2.72  | $1.94 \pm 2.66$   | 3.0 |
| Glycerol derivatives               | 107 11            | <b>7</b> 2.2 |       | 20.4 42.2         | 2.5 |
| Glycerol                           | $107 \pm 14$      | 53.2         | 62.2  | $39.1 \pm 13.3$   | 2.7 |
| Diethylene glycol                  | $34.8 \pm 12.8$   | 25.9         | 29.4  | $6.61 \pm 1.60$   | 5.3 |
| Triethylene glycol                 | $27.3 \pm 16.3$   | 20.3         | 6.48  | nd                | -   |
| Pentadecanoic acid, Glycerine-(1)- |                   | _            | _     |                   |     |
| monoester                          | $11.2 \pm 15.4$   | nd           | nd    | nd                | -   |
| 1-Monopalmitin                     | $259 \pm 139$     | 1.32         | 5.31  | $9.82 \pm 2.18$   | 26  |
| 1-Monostearin                      | $135 \pm 91$      | nd           | 7.77  | $29.5 \pm 3.9$    | 4.6 |
| α-Glyceryl pentadecanoate          | $17.1 \pm 15.2$   | nd           | 1.49  | nd                | -   |
| Phenolic derivatives               |                   |              |       |                   |     |
| 2,4-Di-tert-butylphenol            | $37.0 \pm 21.0$   | 4.68         | bdl   | $6.94 \pm 4.84$   | 5.3 |
| Benzyl alcohol                     | $97.0 \pm 77.0$   | 14.6         | 2.08  | $6.10 \pm 6.89$   | 16  |
| Benzoic acid alkyl esters          | $158 \pm 233$     | 26.8         | 11.0  | $8.68 \pm 14.06$  | 18  |
| Phthalates                         |                   |              |       |                   |     |
| Diethyl Phthalate                  | $4.83 \pm 10.76$  | bdl          | 2.02  | nd                | -   |
| Di-n-butyl Phthalate               | $4.23 \pm 8.35$   | bdl          | 2.70  | $0.279 \pm 0.228$ | 15  |
| Bis(2-ethylhexyl)phthalate         | $39.8 \pm 86.4$   | bdl          | 9.45  | $0.280 \pm 0.362$ | 142 |
| Other phthalates                   | $545 \pm 403$     | 198          | 331   | $104 \pm 166$     | 5.3 |
| Saccharides and polyols            |                   |              |       |                   |     |
| Galactosan                         | $1.02 \pm 1.29$   | 0.984        | 1.27  | $4.10 \pm 2.71$   | 0.2 |
| Mannosan                           | $3.37 \pm 1.93$   | 2.02         | 2.29  | $8.71 \pm 3.29$   | 0.4 |
| Levoglucosan                       | $43.2 \pm 27.2$   | 23.2         | 49.8  | $73.3 \pm 25.4$   | 0.6 |
| Other compounds                    |                   |              |       |                   |     |
| Cholesterol                        | $59.5 \pm 68.1$   | 0.220        | 0.126 | $0.348 \pm 0.383$ | 171 |
| Methyl dihydrojasmonate            | $41.8 \pm 33.8$   | 73.4         | 1.75  | $0.441 \pm 0.278$ | 95  |
| Ethylene brassylate                | $26.7 \pm 26.8$   | 13.6         | 8.92  | $0.637 \pm 0.485$ | 42  |
| Geranylacetone                     | $1.76 \pm 2.63$   | nd           | nd    | nd                | -   |
| Parsol MCX                         | $202 \pm 209$     | 11.9         | 3.69  | $8.88 \pm 11.86$  | 23  |
| Tributyl acetylcitrate             | $8.74 \pm 8.84$   | 2.98         | 1.81  | $0.355 \pm 0.250$ | 25  |
| Tetramethrin                       | $15.2 \pm 34.0$   | nd           | nd    | nd                | -   |
| Oxidised irgafos 168               | $12.6 \pm 20.2$   | 9.82         | nd    | $5.52 \pm 10.93$  | 2.3 |
| Irganox 1086 (Antioxidant 1076)    | $3.18 \pm 7.11$   | bdl          | nd    | $8.64 \pm 11.70$  | 0.4 |
| Vitamin E acetate                  | $32.5 \pm 43.8$   | nd           | nd    | $1.01 \pm 0.73$   | 32  |
| Butylphenyl methylpropional        |                   |              |       |                   |     |
| (lilial)                           | $2.31 \pm 2.95$   | 0.287        | nd    | $0.025 \pm 0.050$ | 93  |
| Farnesyl acetaldehyde              | $14.3 \pm 24.5$   | nd           | nd    | nd                | -   |
| Galaxolide                         | $40.1 \pm 79.4$   | 21.9         | nd    | $0.821 \pm 1.642$ | 49  |
|                                    |                   |              |       |                   |     |

nd – not detected

bdl – below detection limit

Table 3. Organic compounds described in the literature as components of consumer and personal care products detected in the  $PM_{10}$  samples of the present study.

| Compounds                                       | Use  | Reference   |
|---|--|---|
| Dehydroabietic acid,                            | Primary component of rosin, used as adhesive or emulsifier in depilatory wax and cosmetics.  | Liu et al. (2014),                                  |
| isoopimaric acid                                |  | Nilsson et al. (2008)                               |
| Glycerol  | Fragrance ingredient, solvent and humectant in a wide range of hair cosmetics.   | Becker et al. (2019)                                |
| 1-Monopalmitine,<br>1-monostearine              | Added to cosmetic formulations mostly as emollients.   | Arachidonate et al. (2004)                          |
| Cholesterol                                     | Emulsifier in cosmetic skin/hair care products and eye/face makeup formulations.   | Elder (1986)  |
| Benzyl alcohol                                  | Fragrance component in makeup goods, fine fragrances, shampoos, toilet soaps and other toiletries, and in cleaners and detergents.   | Andersen et al. (2001)                              |
| 2,4-Di-tertbutylphenol                          | Synthetic phenolic antioxidant in various personal care products (hair conditioners, hair sprays, shaving gels, face/hand/sun creams, etc.).   | Liu and Mabury (2019)                               |
| Benzoic acid alkyl esters                       | Included in cosmetics as fragrance ingredients, skin-conditioning agents (emollient), skin-conditioning agents (miscellaneous), preservatives, solvents, and plasticisers.   | Becker et al. (2012)                                |
| Parsol MCX                                      | Ingredient in sunscreen hair care formulations (gels or sprays) and skin care products.  | Maillan (2002)                                      |
| Ethylene brassylate,<br>methyl dihydrojasmonate | Fragrance ingredient in cosmetics products (fine fragrances, shampoos, toilet soaps, other toiletries), household cleaners and detergents.   | McGinty et al. (2011)<br>Scognamiglio et al. (2012) |
| Galaxolide                                      | Fixative for retarding the release of other fragrances with higher volatility in synthetic polycyclic musk; ingredient in personal care (body creams, body lotion, shampoo, soap, toothpaste and hair conditioner) and household products. | Correia et al. (2013)                               |
| Acetyl tributyl citrate                         | Used in cosmetic products (hair sprays) and as a plasticiser in vinyl products, adhesives and coatings.  | Johnson (2002)                                      |
| Lilial,   | Fragrance components in cosmetic products (shampoos, hair conditioners, liquid soaps, and wet tissues) and in detergents (multi-purpose cleaners and washing-up liquids).  | Yazar et al. (2011)                                 |
| Oxidised Irgafos 168                            | Antioxidants in the production of plastics.  | Hermabessiere et al. (2020)                         |
| Vitamine E acetate                              | Antioxidant and humectant in a wide range of hair and skin cosmetic products.  | Fiume (2002)  |

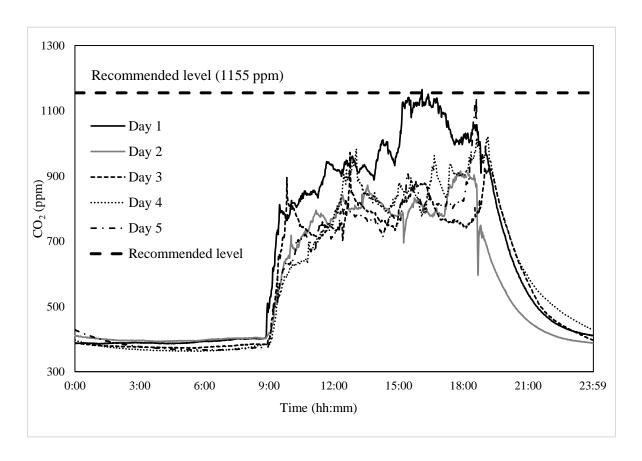


Figure 1. Variation of indoor CO<sub>2</sub> concentrations on weekdays (According to ASHRAE, the recommended level was estimated as 700 ppm above outdoor mean CO<sub>2</sub> concentration).

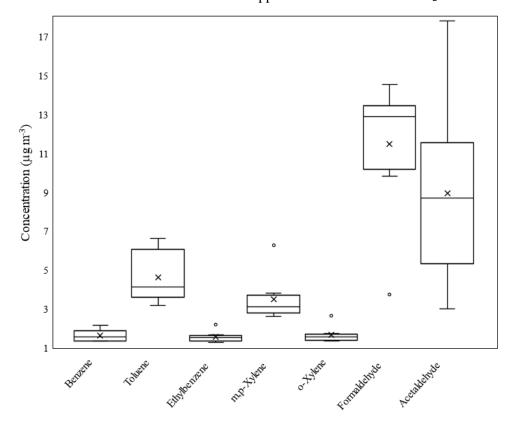


Figure 2. Boxplots for BTEX, formaldehyde and acetaldehyde concentrations ( $\mu g \ m^{-3}$ ) in the indoor air of the beauty salon.

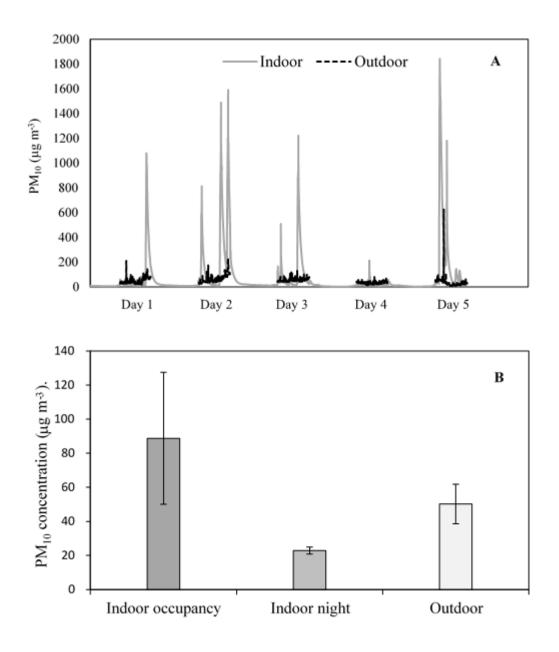


Figure 3. Daily evolution of  $PM_{10}$  concentrations indoors and outdoors during the working time period (9:00-19:00) (A) and mean concentrations of  $PM_{10}$  (B).

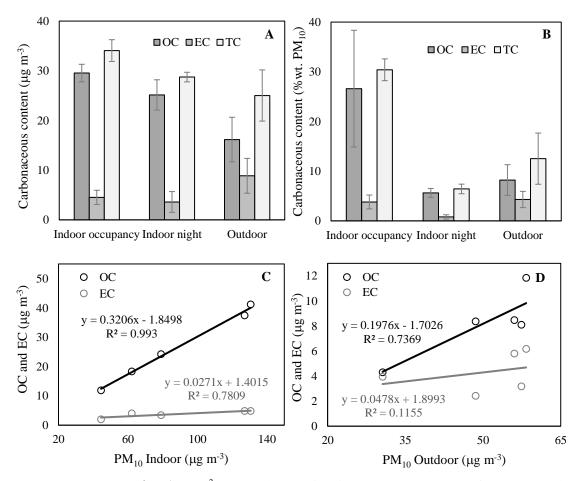


Figure 4.  $PM_{10}$  concentration ( $\mu g \ m^{-3}$ ) (A) and mass fraction (%wt.  $PM_{10}$ ) (B) of OC, EC and TC. Correlations between  $PM_{10}$  concentrations ( $\mu g \ m^{-3}$ ) and its carbonaceous fractions (C, D).

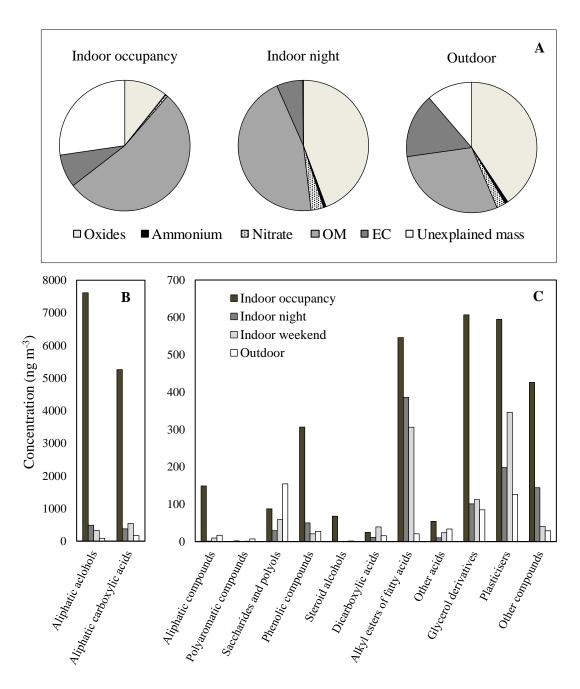


Figure 5. Chemical mass closure of  $PM_{10}$  (A) and total mean concentrations (ng m<sup>-3</sup>) of different classes of  $PM_{10}$ -bound organic compounds.

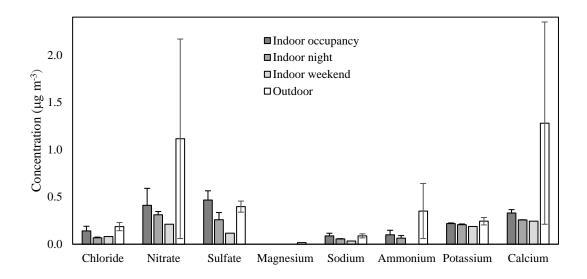


Figure 6. Concentrations (mean  $\pm$  SD) of water-soluble ions (ng m $^{\text{-}3}$ ) in PM  $_{10}.$ 

**SUPPORTING INFORMATION** 

Air quality and particulate matter speciation in a beauty salon and

surrounding outdoor environment: exploratory study

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Health risk assessment

The cancer and non-cancer risks to human health from exposure to toxic substances via

inhalation were calculated according to the methodology established by the United States

Environmental Protection Agency (USEPA, 2009).

The excess cancer risk (CR) attributable to inhalation exposures to carcinogenic species i (e.g.

benzene, formaldehyde, acetaldehyde, Cr, Ni, As and Pb), was estimated as follows:

 $CR_i = EC_i \times IUR_i$ (1)

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where  $EC_i$  is the exposure concentration of compound i (µg m<sup>-3</sup>) and  $IUR_i$  is the inhalation unit risk ((µg m<sup>-3</sup>)<sup>-1</sup>). IUR values were obtained from databases provided by USEPA. In the case of Cr, which was determined as Cr(VI), one seventh of the measured concentration was used to estimate the risk, based on a Cr(VI):Cr(III) proportion of 1/6 and the IUR available for Cr(VI). This metal occurs in the ambient air in the trivalent (Cr(III)) and the hexavalent (Cr(VI)) stable forms. There is not enough data to know if chromium (III) causes cancer. However, according to the USEPA classification, Cr(VI) is considered as a human carcinogen (Group A) by exposure via inhalation route. In the case of PAHs, benzo[a]pyrene equivalent concentrations ( $BaP_{eq}$ ,  $ng m^{-3}$ ) were used to estimate CR. The  $BaP_{eq}$  concentrations were calculated by multiplying each measured concentration of individual PAHs by the respective toxic equivalent factors (TEF) taken from Bari et al. (2010).

The exposure concentration (EC) of a selected compound i was calculated as follows:

$$EC_i = (C_i \times ET \times EF \times ED) / AT$$
 (2)

where  $C_i$  is the measured concentration of compound i (µg m<sup>-3</sup>), ET is the exposure time (8 hours day <sup>-1</sup>), EF is the exposure frequency (48 weeks × 5 days × 8 hours / 24 hours = 80 days year<sup>-1</sup>, by accounting for 5 workdays per week and 4 weeks of vacation per year), ED is the exposure duration (25 years) and AT is the averaging time for 70 years (70 years × 365 days year<sup>-1</sup> × 24 hours day<sup>-1</sup>).

For non-carcinogenic species, the risk was assessed by calculating the Hazard Quotient (HQ) as follows:

$$HQ = EC / RfC$$
 (3)

where  $HQ_i$  is the hazard quotient of compound i, and  $RfC_i$  is the chronic reference concentration of compound i in  $\mu g$  m<sup>-3</sup>. Additionally, the hazard index (HI) was calculated as the sum of the HQ of each individual compound.  $RfC_i$  values were obtained from the databases provided by the Office of Environmental Health Hazard Assessment (OEHHA) and the Integrated Risk

Information System (IRIS) of USEPA (2019). For elements, for which inhalation reference doses are unavailable, RfC values were estimated from the reference doses for oral exposure (RfD) according to the USEPA methodology (USEPA, 2013).

## Supplementary tables and figures

Table S1. Working activities, equipment and products used in the beauty salon during measurements.

|       | Number of occupants (women/men) | Indoor activities<br>(number of offered<br>services)  | Equipment/accessories used   | Products used   | Observations   |
|-------|---------------------------------|---|--|---|--|
| Day 1 | Worker (1)<br>Customers (1/12)  | Hair cut (13)<br>Wash & blow dry (8)<br>Sweeping hair   | Hair cutting machine<br>Scissors<br>Hair dryer   | Shampoo<br>Conditioner  |  |
| Day 2 | Worker (1)<br>Customers (4/3)   | Hair cut (3) Wash & blow dry (7) Cleaning the bathroom Sweeping hair  | Scissors<br>Hair dryer   | Shampoo<br>Conditioner<br>Hair foam<br>Lacquer spray<br>Air freshener spray                           |  |
| Day 3 | Worker (1)<br>Customers (6/2)   | Hair cut (1) Wash & blow dry (4) Manicures (3) Waxing in the next room with the door closed (1) Sweeping hair   | Scissors<br>Hair dryer   | Shampoo<br>Conditioner<br>Hair foam<br>Lacquer spray<br>Wax<br>Manicure products                      |  |
| Day 4 | Worker (1)<br>Customers (3/8)   | Hair cut (5) Wash & blow dry (6) Hair bleaching (1) Hair hydration treatment (1) Manicure (1) Waxing in the next room with the door open (1) Waxing in the next room with the door closed (1) Sweeping hair | Hair cutting machine<br>Scissors<br>Hair dryer<br>Hair steamer<br>UV nail dryer<br>machine | Shampoo<br>Conditioner<br>Curly hair product<br>Wax<br>Hair hydration<br>product<br>Manicure products |  |
| Day 5 | Worker (1)<br>Customers (6/2)   | Wash & blow dry (3) Hair straightening (1) Manicure (1) Waxing in the next room with the door closed (1) Sweeping hair  | Hair cutting machine<br>Scissors<br>Hair dryer<br>Hair straightening iron                  | Shampoo<br>Conditioner<br>Hair gel<br>Lacquer spray<br>Manicure products                              | It rained during the<br>night<br>Construction works<br>across the street |

Table S2. Experimental design.

|   | Sampling loca            | Sampling location            |  | Sampling time (h)                        | Sampling volume (m <sup>-3</sup> )                 | Samples per day | Chemical analysis  |
|---|--------------------------|------------------------------|--|--|--|-----------------|--|
|   | Inside                   | Outside                      |  |  |  |                 |  |
| Comfort parameters,<br>CO and CO <sub>2</sub> | Centre of the salon      | ~ 3 m away<br>from the salon | 5 working<br>days and 1<br>weekend day | Continuous                               | -  | -               | -  |
| VOCs  | Near the wall on a stand | -                            | 3 working days                         | 10                                       | 0.009  | 3               | BTEX   |
| Carbonyls                                     | Near the wall on a stand | -                            | 3 working days                         | 10                                       | 0.216 - 0.303                                      | 3               | FA, ACT <sup>a</sup>   |
| PM <sub>10</sub> (gravimetric method)         | Centre of the salon      | ~ 3 m away<br>from the salon | 5 working<br>days and 1<br>weekend day | 10 (occupancy)<br>14 (non-<br>occupancy) | 14.7 – 18.3 <sup>b</sup><br>182 – 243 <sup>c</sup> | 3 <sup>d</sup>  | Teflon filters - trace elements, water-soluble ions Quartz filters - carbonaceous content, speciation of organic compounds |
| PM (photometric method)                       | Centre of the salon      | ~ 3 m away from the salon    | Continuous                             | Continuous                               | -  | -               | - ^  |

<sup>&</sup>lt;sup>a</sup> FA – formaldehyde, ACT – acetaldehyde.

<sup>&</sup>lt;sup>b</sup> sampling volume for PM<sub>10</sub> samples collected on Teflon filters with high volume air MCV (model CAV-A/mb) instruments.

 $<sup>^{\</sup>text{c}}$  sampling volume for  $PM_{10}$  samples on quartz fibre filters with a TCR TECORA.

<sup>&</sup>lt;sup>d</sup> two indoor samples (occupancy and non-occupancy period) and one outdoor sample (occupancy period).

Table S3. Comfort parameters and CO and CO<sub>2</sub> concentrations.

|         | CO <sub>2</sub> (ppm) |          | CO (ppm)        |           | T (°C)         |           | HR (%)          |           |
|---------|-----------------------|----------|-----------------|-----------|----------------|-----------|-----------------|-----------|
|         | Mean                  | Range    | Mean            | Range     | Mean           | Range     | Mean            | Range     |
| Indoor  | $818 \pm 82$          | 425-1165 | $0.25 \pm 0.26$ | bdl-0.90  | $18.7 \pm 0.7$ | 14.8-21.5 | $39.7 \pm 8.8$  | 28.6-53.2 |
| Night   | $388 \pm 12$          | 362-674  | $0.25 \pm 0.32$ | bdl-1.00  | $16.4\pm1.5$   | 14.6-18.8 | $33.3 \pm 7.8$  | 27.8-50.4 |
| Weekend | $380\pm17$            | 386-414  | $0.12 \pm 0.05$ | 0.10-0.50 | $16.1 \pm 0.8$ | 15.5-17.5 | $31.8 \pm 2.8$  | 28.1-35.3 |
| Outdoor | $455\pm12$            | 420-535  | $0.16 \pm 0.19$ | bdl-0.90  | $9.5 \pm 1.1$  | 2.0-20.4  | $55.9 \pm 21.0$ | 15.5-86.9 |

bdl – below the limit of detection

Table S4. Pearson's correlation coefficients between mean concentrations of BTEX, formaldehyde and acetaldehyde.

|                    | Benzene | Toluene | Ethylbenzene | <i>m/p</i> -Xylene | o-Xylene | Formaldehyde | Acetaldehyde | BTEX   |
|--------------------|---------|---------|--------------|--------------------|----------|--------------|--------------|--------|
| Benzene            | 1       | 0.39    | 0.23         | 0.24               | 0.15     | 0.23         | -0.59        | 0.40   |
| Toluene            |         | 1       | 0.79*        | 0.75*              | 0.76     | -0.36        | -0.30        | 0.92** |
| Ethylbenzene       |         |         | 1            | 0.98**             | 0.98**   | -0.80*       | -0.63        | 0.95** |
| <i>m/p</i> -Xylene |         |         |              | 1                  | 0.99**   | -0.84**      | -0.67        | 0.94** |
| o-Xylene           |         |         |              |                    | 1        | -0.84**      | -0.56        | 0.93** |
| Formaldehyde       |         |         |              |                    |          | 1            | 0.52         | -0.63  |
| Acetaldehyde       |         |         |              |                    |          |              | 1            | -0.57  |
| BTEX               |         |         |              |                    |          |              |              | 1.00   |

<sup>\*</sup>p < 0.05; \*\*p < 0.01

Table S5. Minimum, maximum and mean concentrations of elements (ng m<sup>-3</sup>), enrichment factors and indoor/outdoor ratios.

|    | Indoor (working hours) |      | hours) | Indoor  | Indoor    | oor Indoor Outdoor (working hours) |      |      |      | I/O  |
|----|------------------------|------|--------|---------|-----------|------------------------------------|------|------|------|------|
|    | Min                    | Max  | AVR    | (night) | (weekend) | Min                                | Max  | AVR  | EF   |      |
| Na | 76.4                   | 251  | 143    | 119     | 44.5      | 206                                | 501  | 312  | 0.34 | 0.46 |
| Mg | 64.5                   | 114  | 88.1   | 67.1    | 20.2      | 105                                | 207  | 159  | 0.25 | 0.55 |
| Al | 226                    | 627  | 441    | 331     | 110       | 214                                | 1685 | 1191 | 0.27 | 0.37 |
| Si | 917                    | 1515 | 1132   | 837     | 233       | 687                                | 4500 | 3210 | 0.19 | 0.35 |
| P  | 11.1                   | 15.8 | 13.9   | 5.10    | 4.92      | 24.6                               | 38.1 | 32.5 | 1.06 | 0.43 |
| S  | 287                    | 520  | 414    | 321     | 156       | 442                                | 652  | 543  | 14.0 | 0.76 |
| Cl | 77.5                   | 223  | 168    | 24.4    | 20.4      | 193                                | 569  | 338  | 14.9 | 0.50 |
| K  | 138                    | 215  | 183    | 174     | 52.4      | 194                                | 651  | 433  | 0.30 | 0.42 |
| Ca | 272                    | 1096 | 603    | 154     | 80.0      | 440                                | 3258 | 2209 | 1.30 | 0.27 |
| Ti | 22.7                   | 38.3 | 30.8   | 20.3    | 7.24      | 13.7                               | 90.5 | 61.8 | 0.35 | 0.50 |
| V  | -                      | 1.60 | 0.40   | 0.089   | -         | -                                  | 2.35 | 0.80 | 0.28 | 0.50 |
| Cr | 0.44                   | 3.28 | 1.46   | 0.69    |           | 2.83                               | 7.11 | 5.47 | 3.08 | 0.27 |
| Mn | 3.81                   | 9.08 | 6.23   | 3.64    | 2.50      | 10.1                               | 31.7 | 22.1 | 0.80 | 0.28 |
| Fe | 214                    | 572  | 377    | 157     | 144       | 812                                | 2265 | 1589 | 1.00 | 0.24 |
| Ni | 0.46                   | 2.42 | 1.05   | 0.59    | 0.52      | -                                  | 1.33 | 0.44 | 0.44 | 2.37 |
| Cu | 45.5                   | 140  | 99.2   | 3.52    | 6.01      | 23.1                               | 49.1 | 35.1 | 50.2 | 2.83 |
| Zn | 23.1                   | 31.6 | 26.2   | 13.1    | 8.94      | 26.1                               | 55.2 | 44.2 | 17.2 | 0.59 |
| As | -                      | 3.64 | 1.64   | 0.73    |           | -                                  | 3.15 | 2.07 | 26.9 | 0.79 |
| Se | 0.19                   | 3.11 | 1.64   | 0.65    | 2.46      | 0.76                               | 6.24 | 2.70 | 564  | 0.61 |
| Br | 1.78                   | 18.1 | 10.0   | 2.24    | 1.25      | 3.60                               | 5.10 | 4.49 | 66.1 | 2.22 |
| Rb | -                      | 1.91 | 0.76   | 0.48    | 1.52      | 0.92                               | 11.5 | 6.11 | 0.91 | 0.12 |
| Sr | 3.89                   | 12.6 | 7.16   | 1.34    | 1.74      | 3.68                               | 27.2 | 19.3 | 1.06 | 0.37 |
| Y  | -                      | 1.66 | 0.45   | 0.92    | 0.60      | 0.71                               | 2.80 | 1.63 | 1.82 | 0.28 |
| Zr | -                      | 2.48 | 1.51   | -       | 0.13      | 2.20                               | 8.92 | 5.65 | 0.44 | 0.27 |
| Mo | -                      | 5.58 | 2.47   | 1.14    | 2.81      | 0.45                               | 1.83 | 1.32 | 24.0 | 1.87 |

Table S6. Concentrations (ng  $\mbox{m}^{-3}\mbox{)}$  of organic compounds in  $\mbox{PM}_{10}\mbox{.}$ 

|                        | Indoor                                 | Indoor non | Indoor  | Outdoor                                | I/O      |
|------------------------|--|------------|---------|--|----------|
| 471 1 17               | occupancy                              | occupancy  | weekend | occupancy                              | occupanc |
| Alkanes and alkenes    | 0.160 - 0.212                          | 0.650      | NT 1    | 0.001 . 0.407                          | 0.0      |
| Undecane               | $0.168 \pm 0.312$                      | 0.659      | Nd      | $0.221 \pm 0.497$                      | 0.8      |
| Dodecene               | $0.018 \pm 0.040$                      | 0.168      | Nd      | $0.075 \pm 0.168$                      | 0.2      |
| Dodecane               | $0.031 \pm 0.068$                      | 0.129      | 0.164   | $0.147 \pm 0.139$                      | 0.2      |
| Tridecane              | $0.146 \pm 0.020$                      | 0.070      | 0.172   | $0.063 \pm 0.064$                      | 2.3      |
| Tetradecene            | $0.015 \pm 0.033$                      | bdl        | bdl     | $0.169 \pm 0.378$                      | 0.1      |
| Pentadecane            | Nd                                     | Nd         | bdl     | $0.105 \pm 0.235$                      | -        |
| Hexadecene             | $0.081 \pm 0.115$                      | Nd         | bdl     | $0.077 \pm 0.173$                      | 1.0      |
| Octadecene             | $0.083 \pm 0.051$                      | bdl        | bdl     | $0.133 \pm 0.169$                      | 0.6      |
| Octadecane             | $0.619 \pm 0.798$                      | bdl        | bdl     | bdl                                    | -        |
| Nonadecane             | $1.83 \pm 1.49$                        | bdl        | bdl     | $0.213 \pm 0.292$                      | 8.6      |
| Eicosene               | Nd                                     | bdl        | Nd      | $0.028 \pm 0.062$                      | -        |
| Eicosane               | $4.12 \pm 2.46$                        | Nd         | 0.63    | $1.18 \pm 0.79$                        | 3.5      |
| Heneicosane            | $5.63 \pm 3.92$                        | bdl        | 1.38    | $1.48 \pm 1.04$                        | 3.8      |
| Docosane               | $11.5 \pm 7.52$                        | bdl        | 3.64    | $1.24 \pm 0.58$                        | 9.2      |
| Tricosane              | $24.6 \pm 14.9$                        | bdl        | 1.50    | $0.526 \pm 1.11$                       | 47       |
| Tetracosane            | $30.9 \pm 21.3$                        | bdl        | bdl     | $0.279 \pm 0.623$                      | 111      |
| Pentacosane            | $23.9 \pm 19.9$                        | bdl        | bdl     | $0.166 \pm 0.371$                      | 144      |
| Hexacosane             | $14.1 \pm 13.7$                        | bdl        | bdl     | bdl                                    | -        |
| Heptacosane            | $9.81 \pm 9.25$                        | bdl        | bdl     | $0.206 \pm 0.461$                      | 48       |
| Octacosane             | $5.20 \pm 5.02$                        | bdl        | bdl     | bdl                                    | -        |
|                        | $3.20 \pm 3.02$<br>$3.10 \pm 0.798$    | 4.53       | 0.431   | $9.01 \pm 11.8$                        | 0.3      |
| Squalene               |  |            | bdl     |  |          |
| Nonacosane             | $3.51 \pm 5.42$                        | bdl        |         | $0.321 \pm 0.718$                      | 11       |
| Triacontane            | $4.26 \pm 3.28$                        | Nd         | Nd      | $0.758 \pm 1.38$                       | 5.6      |
| Hentriacontane         | $2.71 \pm 4.06$                        | Nd         | 0.711   | $0.318 \pm 0.711$                      | 8.5      |
| Dotriacontane          | $1.27 \pm 2.92$                        | Nd         | 0.536   | $0.110 \pm 0.247$                      | 12       |
| Tritriacontane         | $0.792 \pm 1.37$                       | Nd         | Nd      | $0.096 \pm 0.215$                      | 8.2      |
| Tetratriacontane       | $0.377 \pm 0.517$                      | Nd         | 0.965   | Nd                                     | -        |
| Pentatriacontane       | $0.176 \pm 0.265$                      | Nd         | Nd      | Nd                                     | -        |
| PAHs                   |  |            |         |  |          |
| Naphthalene            | $0.005 \pm 0.004$                      | 0.016      | bdl     | $0.046 \pm 0.102$                      | 0.1      |
| Acenaphthylene         | $0.314 \pm 0.283$                      | Nd         | Nd      | Nd                                     | -        |
| Acenaphthene           | $0.016 \pm 0.008$                      | 0.012      | Nd      | $0.004 \pm 0.008$                      | 3.7      |
| Fluorene               | $0.012 \pm 0.023$                      | bdl        | bdl     | $0.003 \pm 0.008$                      | 3.3      |
| Phenanthrene           | $0.072 \pm 0.025$                      | 0.028      | 0.024   | $0.259 \pm 0.208$                      | 0.3      |
| Anthracene             | $0.002 \pm 0.003$                      | bdl        | bdl     | $0.015 \pm 0.016$                      | 0.1      |
| Fluoranthene           | $0.141 \pm 0.044$                      | 0.065      | 0.161   | $0.986 \pm 0863$                       | 0.1      |
| Pyrene                 | $0.121 \pm 0.041$                      | 0.037      | 0.131   | $1.01 \pm 0.76$                        | 0.1      |
| Chrysene               | $0.183 \pm 0.117$                      | bdl        | bdl     | $1.03 \pm 0.508$                       | 0.2      |
| Perylene               | $0.031 \pm 0.016$                      | 0.008      | 0.004   | $0.051 \pm 0.027$                      | 0.6      |
| p-Terphenyl            | $0.001 \pm 0.003$                      | Nd         | Nd      | $0.033 \pm 0.036$                      | 0.04     |
| Benzo[a]anthracene     | $0.057 \pm 0.071$                      | bdl        | bdl     | $0.499 \pm 0.311$                      | 0.1      |
| Benzo[b]fluoranthene   | $0.163 \pm 0.096$                      | bdl        | bdl     | $0.669 \pm 0.373$                      | 0.2      |
| Benzo[k]fluoranthene   | $0.103 \pm 0.090$<br>$0.202 \pm 0.189$ | bdl        | Nd      | $0.374 \pm 0.295$                      | 0.5      |
| Benzo[e]pyrene         | $0.202 \pm 0.189$<br>$0.304 \pm 0.101$ | 0.124      | 0.286   | $0.74 \pm 0.293$<br>$0.781 \pm 0.336$  | 0.3      |
| 1 -                    | $0.304 \pm 0.101$<br>$0.209 \pm 0.135$ | bdl        | 0.200   | $0.781 \pm 0.330$<br>$0.521 \pm 0.393$ | 0.4      |
| Benzo[a]pyrene         |  |            |         |  |          |
| Indeno[1,2,3-cd]pyrene | $0.118 \pm 0.067$                      | 0.007      | 0.027   | $0.227 \pm 0.167$                      | 0.5      |
| Dibenzo[a,h]anthracene | $0.009 \pm 0.008$                      | bdl        | Nd      | $0.023 \pm 0.022$                      | 0.4      |
| Benzo[g,h,i]perylene   | $0.130 \pm 0.076$                      | 0.012      | bdl     | $0.286 \pm 0.194$                      | 0.5      |
| Carbazol               | $0.003 \pm 0.007$                      | Nd         | Nd      | $0.023 \pm 0.024$                      | 0.1      |
| Aliphatic alcohols     |  |            |         |  |          |
| 1-Octanol              | $2.24 \pm 2.22$                        | 0.587      | Nda     | $0.023 \pm 0.046$                      | 98       |
| 1-Decanol              | $0.449 \pm 0.351$                      | 0.267      | 0.018   | $0.016 \pm 0.020$                      | 28       |

| 1-Dodecanol                     | $11.4 \pm 6.7$                         | 10.3  | 6.94  | $0.906 \pm 0.547$                      | 13             |
|---------------------------------|--|-------|-------|--|----------------|
| C <sub>13</sub> alcohol isomers | $4.35 \pm 3.40$                        | 6.06  | 5.59  | $4.88 \pm 3.83$                        | 0.9            |
| 1-Tetradecanol                  | $192 \pm 275$                          | 70.9  | 87.2  | $6.37 \pm 2.28$                        | 30             |
| C <sub>14</sub> alcohol isomers | $0.627 \pm 0.749$                      | 1.35  | 1.39  | $6.36 \pm 3.03$                        | 0.1            |
| 1-Pentadecanol                  | $34.3 \pm 18.7$                        | 28.6  | 16.6  | $10.4 \pm 4.27$                        | 3.3            |
| C <sub>15</sub> alcohol isomers | $7.05 \pm 5.32$                        | 7.46  | 4.17  | $10.3 \pm 4.42$                        | 0.7            |
| Hexadecanol                     | $2502 \pm 2413$                        | 247   | 147   | $18.1 \pm 5.25$                        | 138            |
| C <sub>17</sub> alcohol isomers | $16.0 \pm 18.5$                        | 3.70  | 5.07  | $0.519 \pm 0.304$                      | 31             |
| 1-Octadecanol (Stearyl alcohol) | $4689 \pm 4844$                        | 103   | 54.6  | $13.9 \pm 5.05$                        | 338            |
| 1-Nonadecanol                   | $10.8 \pm 11.0$                        | 0.303 | 0.242 | $1.30 \pm 2.00$                        | 8.4            |
| C <sub>20</sub> alcohol isomers | $25.1 \pm 33.3$                        | 4.10  | Nd    | $4.04 \pm 3.90$                        | 6.2            |
| 1-Eicosanol                     | $91.8 \pm 92.8$                        | 0.978 | dlb   | $0.965 \pm 0.890$                      | 95             |
| 1-Heneicosanol                  | $2.37 \pm 2.57$                        | Nd    | Nd    | $0.095 \pm 0.116$                      | 25             |
| 1-Docosanol (Behenyl alcohol)   | $17.5 \pm 20.4$                        | 0.462 | 0.460 | $0.912 \pm 1.04$                       | 19             |
| C <sub>22</sub> alcohol isomers | $0.292 \pm 0.654$                      | Nd    | Nd    | Nd                                     | -              |
| 1-Tricosanol                    | $0.700 \pm 0.653$                      | 0.043 | 0.039 | $0.110 \pm 0.099$                      | 6.4            |
| 1-Tetracosanol                  | $3.78 \pm 2.94$                        | 0.512 | Nd    | $1.73 \pm 0.965$                       | 2.2            |
| 1-Heptacosanol                  | $0.037 \pm 0.024$                      | 0.035 | 0.014 | $0.088 \pm 0.084$                      | 0.4            |
| 1-Octacosanol                   | $0.663 \pm 0.474$                      | 0.033 | 0.190 | $1.83 \pm 1.96$                        | 0.4            |
| 1-Tricontanol                   | $0.166 \pm 0.100$                      | 0.410 | 0.130 | $0.532 \pm 0.656$                      | 0.4            |
| 1-Pentacosanol                  | $0.100 \pm 0.100$<br>$0.208 \pm 0.155$ | 0.120 | 0.031 | $0.332 \pm 0.030$<br>$0.139 \pm 0.123$ | 1.5            |
| 1-Hexacosanol                   | $0.208 \pm 0.133$<br>$1.64 \pm 1.17$   | 1.49  | 1.07  | $5.30 \pm 4.05$                        | 0.3            |
| Steroid alcohols                | 1.04 ± 1.17                            | 1.47  | 1.07  | 3.30 ± 4.03                            | 0.5            |
|                                 | $0.454 \pm 0.348$                      | 0.123 | 0.117 | $0.388 \pm 0.438$                      | 1.2            |
| Stigmasterol                    |  |       | 0.117 |  |                |
| β-Sitosterol                    | $0.638 \pm 0.436$                      | 0.130 | 0.086 | $0.897 \pm 1.29$                       | 0.7            |
| Steroid alcohols                | <b>50.5 60.1</b>                       | 0.000 | 0.10  | 0.240 0.202                            | 171            |
| Cholesterol                     | $59.5 \pm 68.1$                        | 0.220 | 0.126 | $0.348 \pm 0.383$                      | 171            |
| 5-Cholesten-3-ol                | $2.99 \pm 5.11$                        | Nd    | Nd    | $0.031 \pm 0.038$                      | 98             |
| (dihydrocholesterol)            |  |       |       |  |                |
| Lathosterol                     | $4.26 \pm 4.66$                        | Nd    | Nd    | Nd                                     |                |
| Aliphatic carboxylic acids      |  |       |       |  |                |
| 1-Octanoic (caprylic) acid      | $0.720 \pm 0.657$                      | 0.080 | 0.292 | $0.111 \pm 0.044$                      | 6.5            |
| 1-Nonanoic (pelargonic) acid    | $1.085 \pm 0.714$                      | 0.007 | 0.782 | $0.271 \pm 0.279$                      | 4.0            |
| 1-Decanoic (caproic) acid       | $17.2 \pm 15.3$                        | 1.07  | 3.99  | $0.849 \pm 0.518$                      | 20             |
| 1-Undecanoic acid               | $0.525 \pm 0.422$                      | 0.034 | 1.423 | $0.312 \pm 0.165$                      | 1.7            |
| 1-Dodecanoic (lauric) acid      | $25.4 \pm 9.1$                         | 18.2  | 65.7  | $4.66 \pm 1.94$                        | 5.5            |
| 1-Tridecanoic acid              | $3.24 \pm 3.68$                        | 5.59  | 5.85  | $0.548 \pm 0.591$                      | 5.9            |
| C <sub>13</sub> acid isomers    | $11.4 \pm 12.1$                        | Nd    | Nd    | $1.21 \pm 1.52$                        | 9.4            |
| 1-Tetradecanoic (myristic) acid | $1274 \pm 543$                         | 274   | 141   | $26.9 \pm 9.7$                         | 47             |
| C <sub>14</sub> acid isomers    | $69.4 \pm 55.9$                        | 19.8  | 4.73  | Nd                                     | -              |
| Tetradecenoic acid              | $52.9 \pm 40.8$                        | 1.49  | 2.96  | Nd                                     | -              |
| 1-Pentadecanoic acid            | $526 \pm 295$                          | 22.3  | 25.7  | $4.27 \pm 2.05$                        | 123            |
| Pentadecenoic acid              | $46.5 \pm 50.7$                        | Nd    | Nd    | Nd                                     | -              |
| C <sub>15</sub> acid isomers    | $153 \pm 143$                          | 12.5  | 9.78  | Nd                                     | -              |
| 1-Hexadecanoic (palmitic) acid  | $950 \pm 594$                          | 0.067 | 206   | $47.7 \pm 35.1$                        | 20             |
| C <sub>16</sub> acid isomers    | $294 \pm 218$                          | 8.20  | 4.34  | Nd                                     | -              |
| Hexadecenoic acid isomer        | $6.42 \pm 10.27$                       | Nd    | Nd    | Nd                                     | -              |
| 9-cis-Hexadecenoic              | $600 \pm 414$                          | 0.033 | 0.544 | $3.09 \pm 5.59$                        | 194            |
| (palmitoleic)acid               |  |       |       |  |                |
| 1-Heptadecanoic acid            | $145 \pm 94$                           | 0.046 | 7.19  | $1.89 \pm 1.29$                        | 77             |
| C <sub>17</sub> acid isomers    | $217 \pm 139$                          | 4.57  | 11.1  | $6.48 \pm 5.89$                        | 34             |
| Heptadecenoic acid              | $105 \pm 97$                           | Nd    | Nd    | Nd                                     | -              |
| 1-Octadecanoic (stearic) acid   | $210 \pm 116$                          | 0.192 | 42.6  | $62.2 \pm 55.7$                        | 3.4            |
| C <sub>18</sub> acid isomers    | $1.69 \pm 3.77$                        | Nd    | Nd    | Nd                                     | -              |
| cis,cis-9,12-Octadecadienoic    | $56.0 \pm 58.8$                        | 0.138 | 0.896 | $1.73 \pm 2.18$                        | 32             |
| (linoleic) acid                 | 2 2.2 = 2 0.0                          | 2.200 | 2.070 |  | <del>-</del> = |
| cis-9-Octadecenoic oleic acid   | $380 \pm 260$                          | bdl   | 5.21  | $5.85 \pm 5.01$                        | 65             |
| cis-11-Octadecenoic acid        | $20.1 \pm 25.4$                        | Nd    | Nd    | Nd                                     | -              |
| 1-Nonadecanoic acid             | $9.72 \pm 7.03$                        | 0.021 | Nd    | $0.243 \pm 0.198$                      | 40             |
| Nonadeceanoic acid              | $3.42 \pm 4.69$                        | Nd    | Nd    | 0.243 ± 0.198<br>Nd                    | -              |
| 1 10114444441014 4414           | シ・マム ニ マ・リフ                            | 114   | 114   | 114                                    |                |

| 1-Eicosanoic (arachidic) acid   | $19.3 \pm 10.2$                        | 0.264 | 1.31        | $3.08 \pm 2.70$   | 6.3 |
|---------------------------------|--|-------|-------------|-------------------|-----|
| Eicosenoic acid                 | $9.26 \pm 8.10$                        | Nd    | Nd          | Nd                | -   |
| C <sub>21</sub> acid isomers    | $4.47 \pm 3.73$                        | 0.561 | Nd          | $0.399 \pm 0.797$ | 11  |
| 1-Docosanoic (behenic) acid     | $10.8 \pm 5.0$                         | 1.63  | 1.68        | $4.75 \pm 3.66$   | 2.3 |
| C <sub>22</sub> acid isomers    | $0.926 \pm 1.31$                       | Nd    | Nd          | Nd                | _   |
| 1-Tetracosanoic acid            | $19.7 \pm 6.79$                        | 3.54  | Nd          | $6.35 \pm 2.80$   | 3.1 |
| 1-Pentacosanoic acid            | $5.28 \pm 2.84$                        | Nd    | Nd          | $0.318 \pm 0.636$ | 17  |
| 1-Hexacosanoic acid             | $4.98 \pm 4.21$                        | 0.670 | 0.142       | $2.64 \pm 2.83$   | 1.9 |
| C <sub>26</sub> acid isomers    | $0.654 \pm 1.23$                       | Nd    | 0.142<br>Nd | 2.04 ± 2.83<br>Nd | 1.9 |
| 1-Tricosanoic acid              |  |       |             |                   | _   |
|                                 | $2.50 \pm 2.67$                        | Nd    | Nd          | Nd                | -   |
| C <sub>23</sub> acid isomers    | $3.47 \pm 3.12$                        | Nd    | Nd          | Nd                | -   |
| Dicarboxylic acids              | 0.00 4.77                              | 7.06  | 10.04       | 2.07 1.21         | 4.7 |
| Laevulic acid                   | $9.80 \pm 4.77$                        | 7.36  | 10.94       | $2.07 \pm 1.31$   | 4.7 |
| Hydroxybutanedioic (malic) acid | $1.15 \pm 1.20$                        | 1.36  | 11.92       | $3.98 \pm 4.32$   | 0.3 |
| Butanedioic (succinic) acid     | $1.17 \pm 0.97$                        | 0.531 | 7.98        | $4.99 \pm 2.22$   | 0.2 |
| 1,5-Pentanedioic acid           | $5.31 \pm 2.55$                        | bdl   | 3.69        | $1.23 \pm 0.54$   | 4.3 |
| Hexanedioic acid                | $5.34 \pm 4.02$                        | 1.657 | 2.84        | $0.900 \pm 0.238$ | 5.9 |
| Octanedioic acid                | $1.51 \pm 1.52$                        | 0.319 | 0.969       | $0.472 \pm 0.097$ | 3.2 |
| Heptanedioic (pimelic) acid     | $0.389 \pm 0.211$                      | 0.100 | 0.767       | $0.456 \pm 0.156$ | 0.9 |
| Decanedioic (sebacic) acid      | $0.123 \pm 0.168$                      | Nd    | Nd          | $0.289 \pm 0.554$ | 0.4 |
| Hexadecanedioic (thapsic) acid  | $0.011 \pm 0.015$                      | 0.017 | 0.030       | $0.029 \pm 0.032$ | 0.4 |
| Other acids                     |  |       |             |                   |     |
| Glyceric acid                   | $6.50 \pm 5.77$                        | 5.26  | 8.10        | $6.81 \pm 2.08$   | 1.0 |
| Hydracrylic acid                | $8.25 \pm 9.24$                        | 1.20  | 7.73        | $4.32 \pm 2.78$   | 1.9 |
| 3-hydroxybutanoic acid          | $0.427 \pm 0.428$                      | 0.023 | 0.755       | $0.377 \pm 0.338$ | 1.1 |
| 3,4-Dihydroxybutanoic acid      | $0.568 \pm 0.372$                      | 0.547 | 0.334       | $0.665 \pm 0.504$ | 0.9 |
| Cis-Pinonic acid                | $0.426 \pm 0.166$                      | 0.317 | 0.334       | $4.99 \pm 4.14$   | 0.1 |
| Citric acid                     | $0.420 \pm 0.100$<br>$0.042 \pm 0.052$ | 0.121 | 1.20        | $7.85 \pm 10.20$  | 0.1 |
| Pinic acid                      | $0.042 \pm 0.032$<br>$1.11 \pm 0.53$   | 0.121 | 2.85        |                   | 0.1 |
|                                 |  |       |             | $5.52 \pm 2.51$   |     |
| 12-Hydroxystearic acid          | Nd                                     | 0.988 | 1.21        | $14.2 \pm 10.5$   | -   |
| Pimaric acid                    | $3.71 \pm 5.67$                        | Nd    | Nd          | Nd                | -   |
| Abietic acid                    | $0.999 \pm 0.606$                      | 0.006 | Nd          | $0.045 \pm 0.045$ | 22  |
| Isopimaric                      | $15.6 \pm 15.6$                        | 0.063 | 0.066       | $0.095 \pm 0.042$ | 163 |
| Dehydroabietic acid             | $16.3 \pm 18.7$                        | 0.576 | 1.10        | $3.05 \pm 0.83$   | 5.3 |
| 15-Hydroxydehydrohabietic acid  | $0.431 \pm 0.599$                      | Nd    | Nd          | $0.046 \pm 0.093$ | 9.3 |
| Alkyl esters of fatty acids     |  |       |             |                   |     |
| Butyl hexanoate                 | $4.72 \pm 3.62$                        | 6.61  | Nd          | $0.270 \pm 0.401$ | 18  |
| Dodecyl octanoate               | $4.80 \pm 5.46$                        | 3.02  | Nd          | $0.126 \pm 0.183$ | 38  |
| Octan-4-yl dodecanoate          | $9.61 \pm 10.39$                       | 12.7  | 9.68        | $0.505 \pm 0.419$ | 19  |
| Methyl tetradecanoate           | $1.64 \pm 2.87$                        | 5.14  | 8.25        | Nd                | -   |
| Butyl tetradecanoate            | $0.248 \pm 0.342$                      | 4.31  | Nd          | Nd                | -   |
| Methyl hexadecanoate            | $6.98 \pm 8.04$                        | 3.02  | 81.6        | $6.46 \pm 4.10$   | 1.1 |
| Ethyl hexadecanoate             | $0.897 \pm 1.036$                      | 5.36  | Nd          | Nd                | _   |
| 2-Hydroxyethyl hexadecanoate    | $11.4 \pm 11.5$                        | Nd    | Nd          | Nd                | _   |
| Isopropyl hexadecanoate         | $8.42 \pm 12.00$                       | Nd    | 25.1        | $0.845 \pm 0.979$ | 10  |
| Hexadecyl hexadecanoate         | $18.5 \pm 21.1$                        | Nd    | Nd          | $0.270 \pm 0.390$ | 69  |
| Dibutyl hexanedioate            | $5.75 \pm 8.87$                        | Nd    | 2.72        | $1.94 \pm 2.66$   | 3.0 |
| Tetradecyl octanoate            | $7.73 \pm 0.07$<br>$7.73 \pm 11.03$    | Nd    | Nd          | Nd                | -   |
| Glycerol derivatives            | 7.75 ± 11.05                           | ING   | 110         | Nu                |     |
| Glycerol                        | 107 ± 14                               | 53.2  | 62.2        | 20 1 ± 12 2       | 2.7 |
|                                 | $107 \pm 14$                           |       | 62.2        | $39.1 \pm 13.3$   | 2.7 |
| Diethylene glycol               | $34.8 \pm 12.8$                        | 25.9  | 29.4        | $6.61 \pm 1.60$   | 5.3 |
| Triethylene glycol              | $27.3 \pm 16.3$                        | 20.3  | 6.48        | Nd                | -   |
| Pentadecanoic acid, Glycerine-  | $11.2 \pm 15.4$                        | Nd    | Nd          | Nd                | -   |
| (1)-monoester                   |  |       |             |                   |     |
| Heptadecanoic acid, glycerine-  |  |       |             |                   |     |
| (1)-monoester                   | $1.11 \pm 1.54$                        | Nd    | Nd          | Nd                | -   |
| 1-Monopalmitin                  | $259 \pm 139$                          | 1.32  | 5.31        | $9.82 \pm 2.18$   | 26  |
| 2-Monopalmitin                  | $7.19 \pm 16.08$                       | Nd    | Nd          | Nd                | -   |
| 1-Monostearin                   | $135 \pm 91$                           | Nd    | 7.77        | $29.5 \pm 3.9$    | 4.6 |
| Glycerol tricaprolate           | $7.44 \pm 14.55$                       | Nd    | Nd          | Nd                | -   |
|                                 |  |       |             |                   |     |

| α-Glyceryl pentadecanoate                       | $17.1 \pm 15.2$                        | Nd           | 1.49           | Nd                                     | -        |
|---|--|--------------|----------------|--|----------|
| Phenolic derivatives                            |  |              |                |  |          |
| Cresol  | $1.76 \pm 0.12$                        | 0.302        | Nd             | $0.030 \pm 0.059$                      | 60       |
| Pyrocatechol                                    | $0.011 \pm 0.003$                      | 0.001        | 0.001          | $0.003 \pm 0.003$                      | 3.4      |
| 5-Isopropyl-3-Methylphenol                      | $0.060 \pm 0.044$                      | 0.031        | 0.058          | $0.060 \pm 0.072$                      | 1.0      |
| Thymol  | $1.00 \pm 0.63$                        | 0.214        | 0.150          | $0.226 \pm 0.245$                      | 4.4      |
| Resorcinol                                      | $0.115 \pm 0.176$                      | 0.005        | 0.004          | $0.022 \pm 0.021$                      | 5.2      |
| 4-Methyl catechol                               | $0.004 \pm 0.002$                      | 0.001        | 0.001          | $0.002 \pm 0.001$                      | 2.0      |
| 2,6-Dimethoxyphenol                             | $0.001 \pm 0.001$                      | 0.001        | 0.001          | $0.001 \pm 0.001$                      | 1.0      |
| Eugenol   | $0.006 \pm 0.007$                      | 0.001        | bdl            | Nd                                     | -        |
| Methoxy eugenol                                 | $0.003 \pm 0.003$                      | 0.004        | 0.002          | $0.007 \pm 0.004$                      | 0.5      |
| 2,4-Di-tert-butylphenol                         | $37.0 \pm 21.0$                        | 4.68         | bdl            | $6.94 \pm 4.84$                        | 5.3      |
| Pyrogallol                                      | $0.003 \pm 0.002$                      | 0.001        | 0.001          | $0.003 \pm 0.003$                      | 1.1      |
| Isoeugenol                                      | $0.178 \pm 0.100$                      | bdl          | 0.092          | $0.031 \pm 0.061$                      | 5.8      |
| 2-Methoxy-4-propylphenol                        | $0.001 \pm 0.001$                      | 0.001        | 0.002          | $0.003 \pm 0.003$                      | 0.4      |
| 4-Phenylphenol                                  | $0.009 \pm 0.021$                      | Nd           | 0.018          | $0.009 \pm 0.011$                      | 1.0      |
| 4-Octyphenol                                    | $0.062 \pm 0.128$                      | Nd<br>14.6   | Nd             | Nd                                     | -<br>16  |
| Benzyl alcohol                                  | $97.0 \pm 77.0$                        |              | 2.08<br>0.202  | $6.10 \pm 6.89$                        | 2.2      |
| Sinapyl alchol<br>Benzoic acid                  | $0.030 \pm 0.029$                      | 0.013<br>bdl |                | $0.014 \pm 0.026$                      | 0.8      |
|   | $0.165 \pm 0.137$<br>$0.329 \pm 0.115$ | 0.068        | 0.071<br>0.386 | $0.204 \pm 0.189$<br>$1.36 \pm 0.54$   | 0.8      |
| 4-hydroxybenzoic acid Benzoic acid alkyl esters | $0.329 \pm 0.113$<br>$158 \pm 233$     | 26.8         | 11.0           | $8.68 \pm 14.06$                       | 18       |
| 4-tert-Butylphenol                              | $6.60 \pm 4.23$                        | 1.68         | 1.62           | $1.80 \pm 1.67$                        | 3.7      |
| 4-Hydroxybenzoic acid methyl                    | $0.00 \pm 4.23$                        | 1.00         | 1.02           | $1.60 \pm 1.07$                        | 3.7      |
| ester (methylparaben)                           | $0.870 \pm 1.140$                      | 0.408        | 1.01           | $0.079 \pm 0.158$                      | 11       |
| Vanillin  | $0.168 \pm 0.165$                      | 0.400        | 0.082          | $0.079 \pm 0.138$<br>$0.033 \pm 0.059$ | 5.0      |
| Vanillic acid                                   | $0.037 \pm 0.055$                      | 0.020        | 0.002          | $0.033 \pm 0.039$<br>$0.133 \pm 0.092$ | 0.3      |
| Trans-cinnamic acid                             | $0.037 \pm 0.033$<br>$0.133 \pm 0.093$ | 0.023        | 0.112          | $0.133 \pm 0.032$<br>$0.248 \pm 0.129$ | 0.5      |
| 4-Hydroxy-3-methoxycinnamic                     | 0.155 = 0.055                          | 0.013        | 0.112          | 0.2 10 = 0.12)                         | 0.5      |
| (ferulic) acid                                  | $0.040 \pm 0.058$                      | 0.043        | 0.254          | $0.035 \pm 0.049$                      | 1.2      |
| Syringic acid                                   | $0.056 \pm 0.046$                      | 0.034        | 0.401          | $0.060 \pm 0.043$                      | 0.9      |
| Phthalic acid                                   | $0.743 \pm 0.784$                      | Nd           | 2.89           | $1.37 \pm 0.55$                        | 0.5      |
| α-Hexylcinnamaldehyde                           | $2.06 \pm 3.52$                        | 1.12         | Nd             | Nd                                     | _        |
| Phthalates                                      |  |              |                |  |          |
| Diethyl Phthalate                               | $4.83 \pm 10.76$                       | bdl          | 2.02           | Nd                                     | -        |
| Di-n-butyl Phthalate                            | $4.23 \pm 8.35$                        | bdl          | 2.70           | $0.279 \pm 0.228$                      | 15       |
| Bis(2-ethylhexyl)phthalate                      | $39.8 \pm 86.4$                        | bdl          | 9.45           | $0.280 \pm 0.362$                      | 142      |
| Other phthalates                                | $545 \pm 403$                          | 198          | 331            | $104 \pm 166$                          | 5.3      |
| (S)-(-)-β-Citronellol                           | $0.922 \pm 0.871$                      | 1.18         | Nd             | $0.037 \pm 0.046$                      | 25       |
| 2,6-Di-tert-butyl-p-                            |  |              |                |  |          |
| benzoquinone                                    | $1.78 \pm 1.84$                        | bdl          | 2.49           | $0.267 \pm 0.387$                      | 6.7      |
| Benzyl butyl phthalate                          | $0.483 \pm 1.080$                      | bdl          | 0.209          | Nd                                     | -        |
| Bis(2-ethylhexyl) adipate                       | $0.022 \pm 0.049$                      | bdl          | 0.451          | $0.009 \pm 0.018$                      | 2.4      |
| Saccharides and polyols                         |  |              |                |  |          |
| Galactosan                                      | $1.02 \pm 1.29$                        | 0.984        | 1.27           | $4.10 \pm 2.71$                        | 0.2      |
| Mannosan  | $3.37 \pm 1.93$                        | 2.02         | 2.29           | $8.71 \pm 3.29$                        | 0.4      |
| Levoglucosan                                    | $43.2 \pm 27.2$                        | 23.2         | 49.8           | $73.3 \pm 25.4$                        | 0.6      |
| Other compounds                                 |  |              |                |  |          |
| Cis-2-Methylcyclohexanol                        | $0.058 \pm 0.022$                      | 0.029        | Nd             | $0.008 \pm 0.013$                      | 7.4      |
| (S)-(-)β-Citronellol                            | $0.922 \pm 0.871$                      | 1.18         | Nd             | $0.037 \pm 0.046$                      | 25       |
| (1S, 2S, 3R, 5S)-2,3-Pinanediol                 | $0.091 \pm 0.040$                      | 0.158        | 0.027          | $0.032 \pm 0.064$                      | 2.9      |
| Meso-Erythritol                                 | Nd                                     | Nd           | Nd             | $0.047 \pm 0.094$                      | -        |
| 1,2,3-Hexanetriol                               | $0.007 \pm 0.015$                      | Nd           | bdl            | Nd                                     | -        |
| 2,6-Di-tert-butyl-p-                            | $1.78 \pm 1.84$                        | Nd           | 2.49           | $0.267 \pm 0.387$                      | 6.7      |
| benzoquinone Mathyl dibydraigamanata            | 41.0 + 22.0                            | 72.4         | 1 75           | 0.411 + 0.240                          | 05       |
| Methyl dihydrojasmonate                         | $41.8 \pm 33.8$                        | 73.4<br>5.15 | 1.75           | $0.411 \pm 0.249$                      | 95<br>12 |
| 2-Propanol, 1-chloro,phosphate                  | $3.98 \pm 3.72$                        | 5.15         | 2.38           | $0.319 \pm 0.468$                      | 13       |
| 7,9-Di-tert-butyl-1-                            |  |              |                |  |          |
| oxaspiro(4,5)deca-6,9-diene-2,8-dione           | $5.68 \pm 5.28$                        | 1.57         | 7.76           | $1.29 \pm 1.35$                        | 4.4      |
| UIOIIC  | J.00 ± J.20                            | 1.5/         | 7.70           | $1.29 \pm 1.33$                        | 4.4      |

| Anthraquinone                   | Nd                | Nd    | Nd    | $0.682 \pm 0.588$ | -   |
|---------------------------------|-------------------|-------|-------|-------------------|-----|
| Ethylene brassylate             | $26.7 \pm 26.8$   | 13.6  | 8.92  | $0.637 \pm 0.485$ | 42  |
| Geranylacetone                  | $1.76 \pm 2.63$   | Nd    | Nd    | Nd                | -   |
| Parsol MCX                      | $202 \pm 209$     | 11.9  | 3.69  | $8.88 \pm 11.85$  | 23  |
| Tributyl acetylcitrate          | $8.74 \pm 8.84$   | 2.98  | 1.81  | $0.355 \pm 0.250$ | 25  |
| Tetramethrin                    | $15.2 \pm 34.0$   | Nd    | Nd    | Nd                | -   |
| Isodecyl diphenyl phosphate     | $2.91 \pm 1.92$   | 1.51  | Nd    | Nd                | -   |
| Oxidised irgafos 168            | $12.6 \pm 20.2$   | 9.82  | Nd    | $5.52 \pm 10.93$  | 2.3 |
| Irganox 1086 (Antioxidant 1076) | $3.18 \pm 7.11$   | nd    | Nd    | $8.64 \pm 11.70$  | 0.5 |
| Vitamin E acetate               | $32.5 \pm 43.8$   | Nd    | Nd    | $1.01 \pm 0.73$   | 32  |
| (±)-a-Tocoferol (Vit, E)        | $0.014 \pm 0.026$ | Nd    | 0.005 | $0.009 \pm 0.011$ | 1.6 |
| 5-oxo-L-proline                 | $5.13 \pm 3.21$   | Nd    | 2.77  | Nd                | -   |
| Lilial                          | $2.31 \pm 2.95$   | 0.287 | Nd    | $0.025 \pm 0.050$ | 93  |
| Farnesyl acetaldehyde           | $14.3 \pm 24.5$   | Nd    | Nd    | Nd                | -   |
| Galaxolide                      | $40.1 \pm 79.4$   | 21.9  | Nd    | $0.821 \pm 1.642$ | 49  |
| Lupeol                          | $0.233 \pm 0.148$ | 0.254 | 0.170 | $0.647 \pm 0.632$ | 0.4 |
| Tetradecanal                    | $3.77 \pm 4.44$   | 0.535 | 8.75  | $0.075 \pm 0.150$ | 50  |
| Isophorone                      | $0.004 \pm 0.008$ | bdl   | bdl   | $0.056 \pm 0.125$ | 0.1 |

nd - not detected.

bdl - below detection limit.

Table S7. Mean risks from inhalation exposure to carcinogenic and noncarcinogenic VOCs.

| Compounds    | CRa) (mean)                | CR (min)              | CR (max)                   | $HQ^{b)}$ (min)            | HQ (mean)                  | HQ (max)                   |
|--------------|----------------------------|-----------------------|----------------------------|----------------------------|----------------------------|----------------------------|
| Benzene      | $8.32 \times 10^{-7}$      | $6.89 \times 10^{-7}$ | $1.10 \times 10^{-6}$      | $4.20\times10^{\text{-}2}$ | $3.48 \times 10^{-2}$      | $5.57 \times 10^{-2}$      |
| Toluene      | -                          | -                     | -                          | $7.57\times10^{\text{-5}}$ | $6.26\times10^{\text{-}5}$ | $1.00\times10^{\text{-4}}$ |
| Ethylbenzene | $1.01\times10^{\text{-}7}$ | $8.34 \times 10^{-8}$ | $1.42 \times 10^{-7}$      | $8.10\times10^{-6}$        | $6.67\times10^{-6}$        | $1.14\times10^{\text{-5}}$ |
| o-Xylene     | -                          | -                     | -                          | $4.30\times10^{\text{-4}}$ | $3.48 \times 10^{-4}$      | $6.90\times10^{\text{-4}}$ |
| m,p-Xylene   | -                          | -                     | -                          | $9.12\times10^{\text{-4}}$ | $6.81 \times 10^{-4}$      | $1.64 \times 10^{-3}$      |
| Formaldehyde | $4.50\times10^{\text{-}6}$ | $1.47 \times 10^{-6}$ | $5.69\times10^{\text{-}6}$ | $3.33\times10^{\text{-2}}$ | $1.09\times10^{\text{-2}}$ | $4.22\times10^{\text{-}2}$ |
| Acetaldehyde | $6.31\times10^{\text{-}7}$ | $2.10 \times 10^{-7}$ | $1.26\times10^{\text{-}6}$ | $2.60 \times 10^{-2}$      | $8.65\times10^{\text{-}3}$ | $5.17 \times 10^{-2}$      |
| $\sum$       | $6.06 \times 10^{-6}$      | -                     | -                          | $1.03 \times 10^{-1}$      | _                          | -                          |

a) CR – excess cancer risk. USEPA guideline  $1 \times 10^{-6}$  for negligible cancer risk; values between  $1 \times 10^{-4}$ 

Table S8. Mean risks from inhalation exposure to PM<sub>10</sub>-bound metals, trace elements and PAHs.

| Compounds   | Risk        | Range (min-max) / Values                     |
|---|-------------|--|
| Metals (Cr, Ni, As, Pb)                                       | CR          | $6.94 \times 10^{-10} - 4.58 \times 10^{-7}$ |
| PAHs  | CR          | $7.60\times 10^{-10} - 1.33\times 10^{-8}$   |
| Trace elements (Al, V, Mn, Fe, Cu, Zn, Se, Sr, Zr)            | HQ          | -  |
| PM <sub>10</sub> -bound metals                                | $\sum$ (CR) | $6.50 \times 10^{-7}$                        |
| PM <sub>10</sub> -bound PAHs                                  | $\sum$ (CR) | $8.13 \times 10^{-9}$                        |
| PM <sub>10</sub> -constituents (metals, trace elements, PAHs) | $\sum$ (CR) | $9.34 \times 10^{-6}$                        |

and  $1 \times 10^{-6}$  suggest a "possible risk". b) HQ – noncancer hazard quotient. It expresses whether the exposure is higher (> 1) or lower (< 1) than the maximum exposure in which there is no effect on human health.

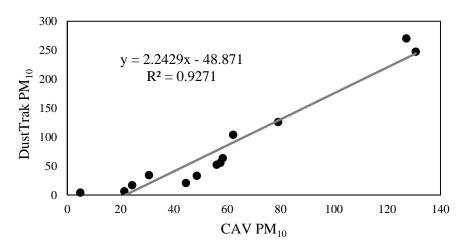


Figure S1. Relationship between the photometric and gravimetric PM measurements.

## **References:**

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