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Comparison of Chinese Herbal Oils and Lemon Oil for Formation of Secondary Organic Aerosol

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ABSTRACT

Several studies reported that evaporation of fragrant essential oils in an indoor environment may cause the emission of secondary organic aerosols (SOAs). However, the tendency of forming SOAs from the use of Chinese herbal oils has not been reported. This study investigated the formation of SOAs from various Chinese herbal oils when reacting with ozone in a controlled environment chamber under different test conditions. Lemon oil, a fragrant essential oil, was also tested under the identical experimental conditions for comparison. The results showed that the formation of SOAs from Chinese herbal oils was limited, compared with lemon oil. Of the Chinese herbal oils tested, Chinese mulberry and perillae folium oils produced more SOAs than the other oils. GC/MS analysis of the essential oils demonstrated the presence of SOA precursors, such as *d*-limonene, in Chinese mulberry and perillae folium oils but not in the other Chinese herbal oils. Compared with the tested Chinese herbal oils, evaporation of 1 mL lemon oil in the presence of 30 ppb ozone may cause an increase of 6.4 μg/m^3 in indoor PM level in a typical room or office. This study concluded that the use of Chinese herbal oils tested in this study would result in a lower particle concentration in indoor settings compared with fragrant essential oils.

***Keywords*:** Secondary organic aerosol (SOA); Particulate matter (PM); Chinese herbal oil; Fragrant essential oil; Aromatherapy.

INTRODUTION

Different types of essential oils have been used in aromatherapy, a treatment aimed at alleviating psychological and physical disorders. Currently, the most common application/administration methods for essential oils are inhalation and external applications such as massage, baths and compresses (Dunning, 2005). The popularity of essential oils in Taiwan over the past few years has increased and can be observed by the emerging number of spa centers, which offer massage therapy using essential oils. In addition to massage therapy in spa centers, use of essential oils is also commonly seen in offices and residences to generate pleasant odors or provide anti-bioactivity benefits (Lahlou, 2004). The essential oils commonly used in Taiwan are classified into two types, *i.e.*, fragrant oils such as lemon and lavender, and Chinese herbal oils such as ginseng and bupleuri. Chinese herbal oils are mainly used for therapeutic purposes while fragrant oils are used for both fragrance and therapeutic purposes. Therefore, both Chinese herbal oils and fragrant oils are seen in either spa centers for massage therapy or indoor settings for therapeutic purposes or other benefits.

Studies have shown that the use of essential oils and products containing fragrances is likely to release various volatile organic compounds (VOCs) into indoor air (Su *et al.*, 2007). The products of VOC degradation following reaction with hydroxyl (OH), nitrate radicals (NO_3) or ozone (O_3), rather than some primary emissions, may cause symptoms such as eye and airway irritation (Wolkoff and Nielsen, 2001; Carslaw and Wolkoff, 2006). Secondary organic aerosols (SOAs) in ultrafine ranges (particles < 100 nm) can be produced as a result of these reactions and contribute a portion of the organic component of $PM_{2.5}$ (Offenberg *et al.*, 2011). Many SOA studies involving fragrances containing *d*-limonene, an identified SOA precursor, have previously been conducted (Vartiainen *et al.*, 2006). However, particle formation from the use of essential oils extracted from Chinese herbs has not been studied. To date, very limited information is available on human exposure to freshly emitted ultrafine particles (UFP) (Kaminsky, *et al.*, 2009). Many studies involving particulate matter or UFP are largely restricted to the vehicular emission (Cheng and Li, 2010; Cheng and Lin, 2010; Geiss *et al*., 2010). Given the popularity of aromatherapy in Taiwan, the SOA-formation capability of essential oils is worthy of more concerns for the future assessment of health impact involving aromatherapy industry.

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The purpose of this work is to determine the SOA-formation capability of various Chinese herbal oils and to compare such capability with that of lemon oil which contains *d*-limonene.

MATERIALS AND METHODS

Experiments were conducted in a small chamber (0.5 m × 0.5 m × 0.5 m) nested inside a larger walk-in environmental chamber (2.2 m × 2.2 m × 2.3 m). Both chambers were made of stainless steel and the interior surfaces of the small chamber were coated with Teflon. Inside the small chamber, two fans are mounted on the top to enhance mixing of gases. Two small openings on the opposite side of the small chamber served as the air inlet and outlet. Another two openings in the small chamber served as the injection port of ozone and sampling port of particles. Air change rate (ACH) in the small chamber was determined by the sulfur hexafluoride (SF_6) decay test and ACH of 0.2 was obtained. Lemon oil (*Citrus limon*) and seven Chinese herbal oils, Chinese mulberry (*Morus australis*), perillae folium (*Perilla frutescens*), ligusticum (*Ligusticum chuangxiong*), angelica (*Angelica archangelica*), penoy (*Paeonia suffruticosa*), dried tangerine peel (*Citrus reticulata*), notopterygium root (*Notopterygii rhizome*), were selected for the study. Bulk samples of these essential oils were analyzed by an Agilent 6890/5973 GC/MSD (Agilent Technologies, Santa Clara, CA, USA) to identify their chemical compositions with ionization achieved by electron impact at 70 eV. The operating conditions were: injection port temperature, 280°C; interface temperature, 280°C. Helium was used as the carrier gas at a flow rate of 1.0 mL/min and the oven temperature was held at 40°C for five minutes, ramped at 2 °C/min to 260°C and held for 10 minutes. For quantitative analysis, the air samples were desorbed and analyzed by a thermal desorption system (Perkin-Elmer, ATD 400) and a gas chromatography (Agilent, 6890/GC). Desorption was performed at 300°C for 10 minutes. The cold trap was kept at –3°C during tube desorption and the sample was thereafter desorbed from the cold trap by heating it to 300°C for three minutes. Nitrogen gas was used as the carrier gas and a HP-1 column (30 m × 0.32 mm I.D. × 0.25 μm) was used. The column temperature was held at 40°C for five minutes, after which it was raised to 100°C for two minutes, and then increased to 200°C where it was held for two minutes.

To minimize background particle concentration, the small chamber was opened during the period when the large chamber was thoroughly ventilated in each set of experiment. Temperature and relative humidity (RH) in the chamber were maintained at 25°C and 55%, respectively. Particle number and mass concentration were measured by a TSI model 3934 scanning mobility particle sizer (SMPS, TSI Inc., St. Paul, MN, USA). After measuring background particle number concentration, a 12-mL bottle filled (with the opening of 0.2-cm in diameter) with essential oil was placed in the small chamber (with door closed) to allow for evaporation. Particle concentration was measured 10 minutes after the oil was evaporated to assess the particle formation capability of the essential oil vapor. After this measurement, ozone produced by an ozone generator (model YW203, Yojin Inc., Taiwan) was injected into the small chamber through Teflon tubing (0.25 inch O.D., 0.125 inch I.D.) and the initial ozone concentration was maintained at approximately 120 ppb. The measurement of particle concentration in the presence of ozone was repeated four times. The amount of essential oil evaporated into the air was recorded by the mass loss before and after each series of experiments. Experiments on each essential oil were repeated three times under the same conditions. For comparison, experiments were conducted using lemon oil with ozone level of 30, 60 and 120 ppb, respectively, in the same protocol.

RESULTS AND DISCUSSION

The average number concentrations of particles ranging in sizes from 26 to 600 nm obtained from essential oils under different test conditions are plotted in Fig. 1. It can be seen that particle number concentrations in background air and in the presence of oil vapor for all the essential oils tested, except lemon oil, were largely unchanged. Statistical test indicated a significant increase of particle number concentration when lemon oil was evaporated ($p = 0.002$). When those essential oils were presented with 120 ppb of ozone, lemon oil was observed to have a substantial increase of particle number concentration ($p < 0.001$) and Chinese mulberry ($p = 0.011$) and perillae folium ($p = 0.002$) were the only two Chinese herbal oils with a significant increase in concentration. Table 1 lists the major constituents and the respective percentages of all essential oils obtained from GC/MS analysis. It can be seen that lemon oil contained terpenes such as limonene, α-pinene and β-pinene, which Hoffmann identified as SOA precursors (*i.e.*, unsaturated compounds) (Hoffmann *et al.*, 1997). No such SOA precursors were found in the Chinese herbal oils with the exception of Chinese mulberry and perillae folium oils which contained relatively small amounts of limonene. The results of the qualitative analysis coincided with the observed increase of particle concentration (Fig. 1) when ozone was presented with Chinese mulberry and perillae folium oils.

The high particle number concentration obtained from the chemical reaction between ozone and lemon oil was in agreement with those reported in the literature (Vartiainen *et al.*, 2006). These results clearly indicated that fragrant essential oils containing SOA precursors can produce significantly high level of particles when they are reacted with a strong oxidant, such as ozone. As Chinese mulberry and perillae folium contain only small amounts of d-limonene, the number of particles generated were fewer than that from lemon oil but exceeded that from the oils without identified SOA precursors. Although some unsaturated compounds, such as linoleic acid, palmitic acid and ethyl linolenate were also found as major constituents in the Chinese herbal oils, no noticeable formation of SOAs was observed in the presence of ozone. Compared with some identified SOA precursors, linoleic acid, palmitic acid and ethyl linolenate are characterized by high molecular weight and low volatility. Such lower gas phase concentration is likely to result in a significantly lower number of SOAs which is observed in the current study.

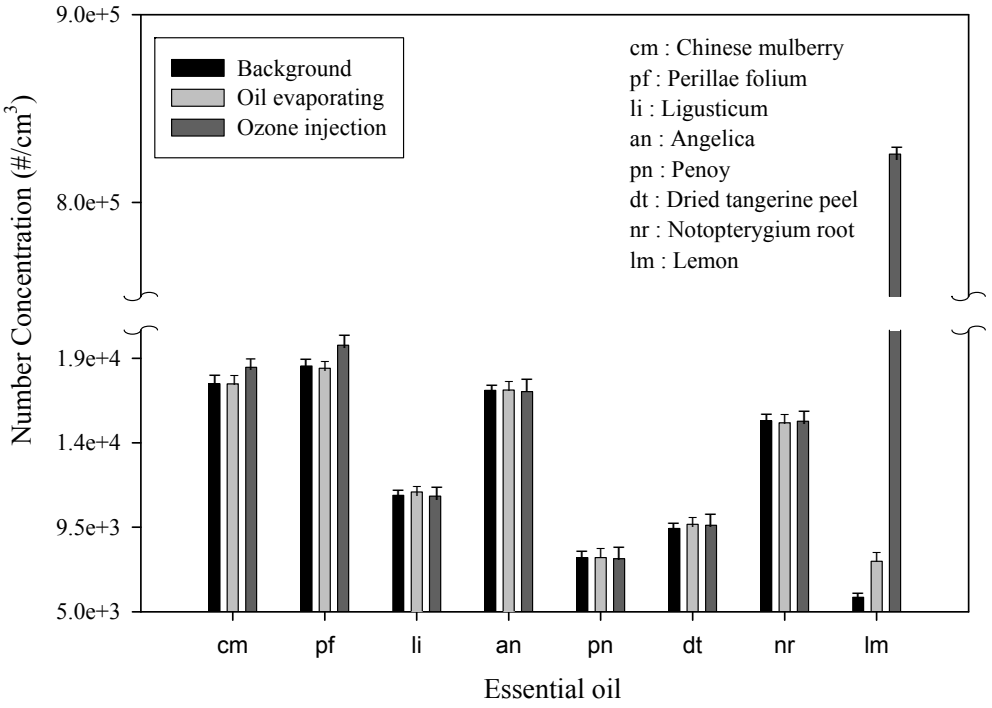

Fig. 1. Average number concentration of essential oil-originated particles under different test conditions.

Table 1. Major constituents of the essential oils tested by GC/MS.

Essential oil	Constituents (Percentage)
Lemon	limonene[a] (71.7%), β-pinene[a] (15.6%), α-pinene[a] (1.9%)
Chinese mulberry	ethyl palmitate (20.6%), ethyl linolenate (18.9%), phytol (13.3%), limonene[a] (2.9%)
Perillae folium	2-butanoyl furan (23.4%), ethyl linolenate (22.2%), ethyl palmitate (11.1%), limonene[a] (1.5%)
Ligusticum	ethyl linoleate (38.3%), beta-methyl benzenepropanal (16.7%), m-cresol (13.7%)
Angelica	ethyl linoleate (36.2%), ethyl palmitate (14.0), ethyl oleate (6.3%)
Penoy	Paeonol (88.1%), benzoic acid (10.0%), ethyl linoleate (0.9%)
Dried Tangerine peel	5-hydroxymethylfurfural (27.9%), methyl-α-D-galactopyranoside (23.0%), pentafluorobenzoic acid (10.9%)
Notopterygium root	2,3-dimethyl-3-phenylcyclopropene (14.5%), 4,6-dimethoxy-3(2H)-benzofuranone (13.6%), (4-methyl-1-methylenepent-4-enyl)benzene (8.1%)

[a] Identified SOAs precursor by Hoffmann *et al*. (1997).

In order to identify the major size range of SOAs generated from the reaction between ozone and the essential oils containing limonene, the particle sizes which ranged from 26 nm to 600 nm were classified into four size ranges. Table 2 shows the particle number concentrations of different size ranges under various conditions and yield ratios for the oils containing limonene. Yield ratio is defined as the ratio of particle number concentration in the presence of ozone to that in the presence of oil vapor only. As shown in Table 2, yield ratios obtained from lemon oil were much greater than those from Chinese mulberry and perillae folium oils, regardless of particle size ranges. For Chinese mulberry and perillae folium oils, the yield ratios of particles smaller than 100 nm were greater than those of particles larger than 100 nm. A similar trend was also observed in lemon oil. Based on the yield ratios obtained from lemon oil and two Chinese herbal oils, the SOAs which originated from these essential oils were generally smaller than 100 nm, i.e., UFPs. Sarwar and Corsi (2007) reported that a burst of particle number concentration containing particles ranging between 20 and 100 nm was found in the initial stage of the ozone/limonene reaction. It was speculated that the majority of SOAs from the reaction between ozone and terpenes were initially formed in sizes smaller than 50 nm and grew over time creating an effective particle growth "wave" as described by Sarwar and Corsi (2007).

Fig. 2 shows the particle number concentrations obtained from the reaction between lemon oil and different levels of ozone. As seen, the presence of lemon oil vapor (*i.e.*, before ozone injection) resulted in a significantly higher particle concentration ($p < 0.001$) than the background air. Compared to the condition of lemon oil vapor only, lemon oil vapor in the presence of ozone resulted in a significant increase of particle concentration ($p < 0.001$) and the increase elevated as ozone level increased. This trend is supported by the work by Lamorena and Lee (2008). When ozone level

Table 2. Particle number concentration (#/cm^3) in different size ranges under various conditions and yield ratios for essential oils containing limonene.

Essential oil	Conditions	26–50 nm	50–100 nm	100–300 nm	300–600 nm	Total count (standard dev.)
Lemon	Background	1202	1916	2200	450	5768 (221)
	Evaporating	2473	2187	2507	524	7691 (356)
	Ozone	475404	327535	21891	973	825803 (5449)
	Yield ratio	192.2	149.8	8.7	1.9	
Chinese mulberry	Background	4468	6345	6208	517	17538 (243)
	Evaporating	4530	6205	5865	534	17134 (397)
	Ozone	5065	6485	6052	540	18142 (228)
	Yield ratio	1.12	1.05	1.03	1.01	
Perillae folium	Background	6974	7236	4163	532	18952 (197)
	Evaporating	6547	6963	4125	509	18144 (286)
	Ozone	7024	7380	4264	525	19193 (256)
	Yield ratio	1.07	1.06	1.03	1.03	

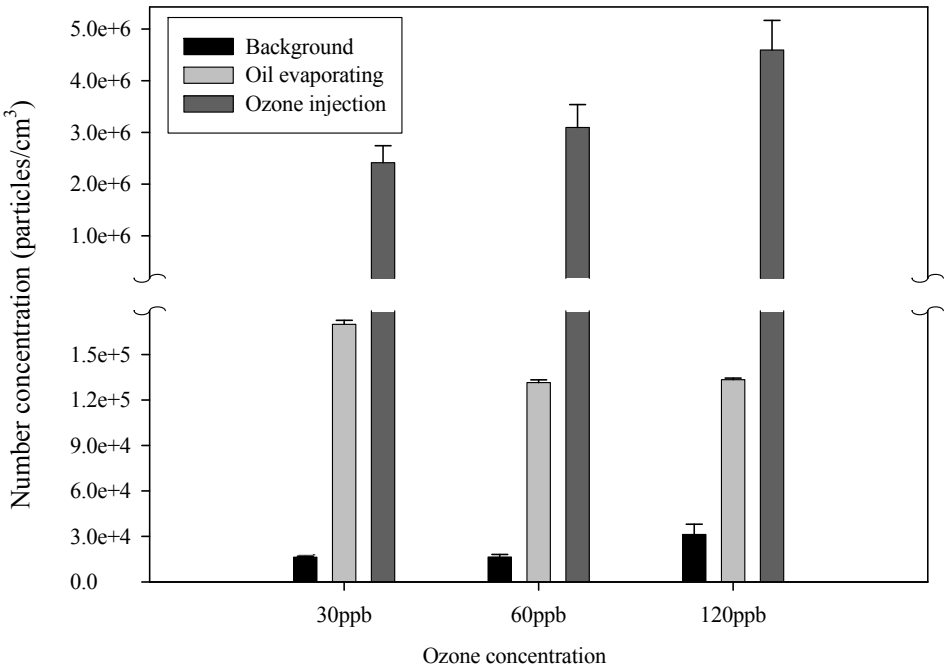

Fig. 2. Average particle number concentration from reactions of lemon oil and different levels of ozone.

was 30 ppb, the generation of UFP was still considerable. Based on our calculation, approximately 0.29 mg of particulate matter was produced when 1 mL of lemon oil was presented with 30 ppb of ozone in the small chamber, with the evaporation rate of approximately 20 μg per minute. This means that a room or an office (approximately 45 m^3) using 1 mL of lemon oil may cause an increase of 6.4 μg/m^3 in PM level. Furthermore, an one-hour massage service using 20 mL of lemon oil will generate 5.8 mg of particulate matter in a spa center. However, this simulation is likely an underestimation of the scenario in offices or spa centers. When essential oils are applied in offices or residences, oil vapors are generated either by heating or by an ultrasonic aromatherapy atomizer/fumigator. Moreover, increased evaporation of essential oil is likely when essential oil is applied onto the human body during massage in spa centers. Therefore, more amount of essential oil will be evaporated and a greater amount of particulate matter will be produced when a room or a spa center using essential oil, such as lemon oil, in the condition of elevated ozone level and/or poor ventilation.

As an elevated particle concentration has been reported in the indoor environment when fragrances are present (Wainman *et al.*, 2000), a much higher PM level may be encountered indoors when outdoor ozone concentration is high or when ozone-emitting office equipment or appliances are present. Ozone-emitting office equipment includes printers, photocopiers and all-in-one office machines (Brown, 1999; Wolkoff, 1999; Lee *et al.*, 2001; Lee and Hsu, 2007). Due to the small sizes of most SOAs which originate from essential oils, a very small increase in PM level indicates the production of a significant number of fine and ultrafine

particles. The adverse health effects resulting from exposure to UFPs have increasingly gained attention over the past few years. With a greater surface area, UFPs can carry large amounts of adsorbed pollutants, oxidant gases, organic compounds, and transition metals (Oberdörster, 2001). These characteristics of UFPs and their increased pulmonary deposition efficiency are considered important in cardiopulmonary toxicity (Gwinn and Vallyathan, 2006). In addition, several epidemiologic studies have confirmed an association between the exposure to fine particles and increased cardiovascular mortality (Pope *et al.*, 2004; Dockery *et al.*, 2005; Nel, 2005). Moreover, one study has shown that the development of childhood asthma was related to the use of various cleaning materials and fragrances in homes (Sherriff *et al.*, 2005). Based on the results of the current study, use of essential oils should be more cautious and Chinese herbal oils are of less influence, compared with fragrant essential oils, with respect to the formation of SOAs. Additionally, ozone sources such as ozone-emitting office equipment or appliances should be avoided when essential oils are applied.

CONCLUSIONS

This study concludes that most of the Chinese herbal oils tested in this study were relatively incapable of producing SOAs in the indoor environment even in the presence of ozone. However, some Chinese herbal oils, such as Chinese mulberry and perillae folium, which contain limonene may produce slightly more SOAs than those containing no identified SOA precursors. Therefore, the use of Chinese herbal oils in an indoor environment, such as offices and spa centers, would result in fewer SOAs than fragrant essential oils under similar condition.

REFERENCES

Brown, S.K. (1999). Assessment of Pollutant Emissions from Dry-Process Photocopiers. *Indoor Air* 9: 259–267.

Carslaw, N. and Wolkoff, P. (2006). A New European Initiative for Indoor Air Pollution Research. *Indoor Air* 16: 4–6.

Cheng, Y.H. and Li, Y.S. (2010). Influences of Traffic Emissions and Meteorological Conditions on Ambient PM_{10} and $PM_{2.5}$ Levels at a Highway Toll Station. *Aerosol Air Qual. Res*. 10: 456–462.

Cheng, Y.H. and Lin, Y.L. (2010). Measurement of Particle Mass Concentrations and Size Distributions in an Underground Station. *Aerosol Air Qual. Res*. 10: 22–29.

Dockery D.W., Luttmann-Gibson H, Rich, D.Q., Link M.S., Mittleman, M.A., Gold, D.R., Koutrakis, P., Schwartz, J.D. and Verrier, R.L. (2005). Association of Air Pollution with Increased Incidence of Ventricular Tachyarrhythmias Recorded by Implanted Cardioverter Defibrillators. *Environ. Health Perspect.* 113: 670–674.

Dunning, T. (2005). Applying a Quality Use of Medicines Framework to Using Essential Oils in Nursing Practice. *Complement. Ther. Clin. Pract.* 11: 172–181.

Geiss, O., Barrero-Moreno, J., Tiredi, S. and Kotzias, D. (2010). Exposure to Particulate Matter in Vehicle Cabins of Private Cars. *Aerosol Air Qual. Res*. 10: 581–588.

Gwinn, M.R. and Vallyathan, V. (2006). Nanoparticles: Health Effects—Pros and Cons. *Environ. Health Perspect.* 114: 1818–1825.

Hoffmann, T., Odum, J.R., Bowman, F., Collins, D., Klockow, D., Flagan, R.C. and Seinfeld, J.H. (1997). Formation of Organic Aerosols from the Oxidation of Biogenic Hydrocarbons. *J. Atmos. Chem.* 26: 189–222.

Kaminsky, J.A., Gaskin, E.A.L.M. Matsuda, M. and Miguel, A.H. (2009). In-Cabin Commuter Exposure to Ultrafine Particles on Commuter Roads in and around Hong Kong's Tseung Kwan O Tunnel. *Aerosol Air Qual. Res*. 9: 353–357.

Lahlou, M. (2004). Essential Oils and Fragrance Compounds: Bioactivity and Mechanisms of Action. *Flavour Fragr. J.* 19: 159–165.

Lamorena, R.B. and Lee, W. (2008). Influence of Ozone Concentration and Temperature on Ultrafine Particle and Gaseous Volatile Organic Compound Formations Generated during Ozone-initiated Reactions with Emitted Terpenes from a Car Air Freshner. *J. Hazard. Mater.* 158: 471–477.

Lee, C.W. and Hsu, D.J. (2007). Measurements of Fine and Ultrafine Particles Formation in Photocopy Centers in Taiwan. *Atmos. Environ.* 41: 6598–6609.

Lee, S.C., Lam, S., and Fai, H.K. (2001). Characterization of VOCs, Ozone, and PM_{10} Emissions from Office Equipment in an Environmental Chamber. *Build. Environ.* 36: 837–842.

Nel, A. (2005). Air Pollution-related Illness: Effects of Particles. *Science* 308: 804–806.

Oberdörster, G. (2001). Pulmonary Effects of Inhaled Ultrafine Particles. *Int. Arch. Occup. Environ. Health* 74: 1–8.

Offenberg, J.H., Lewandowski, M., Jaoui, M. and Kleindienst, T.E. (2011). Contributions of Biogenic and Anthropogenic Hydrocarbons to Secondary Organic Aerosol during 2006 in Research Triangle Park, NC. *Aerosol Air Qual. Res*. 11: 99–108.

Pope, C.A. III, Burnett, R.T., Thurston, G.D., Thun, M.J., Calle, E.E., Krewski, D. and Godleski, J.J. (2004). Cardiovascular Mortality and Long-term Exposure to Particulate Air Pollution: Epidemiological Evidence of General Pathophysiological Pathways of Disease. *Circulation* 109: 71–77.

Sarwar, G. and Corsi, R. (2007). The Effects of Ozone/ Limonene Reactions on Indoor Secondary Organic Aerosols. *Atmos. Environ.* 41: 959–973.

Sherriff, A., Farrow, A., Golding, J., Henderson, J., the ALSPAC Study Team and Hendersen, J. (2005). Frequent Use of Chemical Household Products Is Associated with Persistent Wheezing in Pre-school Age Children. *Thorax* 60: 45–49.

Su, H.J., Chao, C.J., Chang, H.Y. and Wu, P.C. (2007). The Effects of Evaporating Essential Oils on Indoor Air Quality. *Atmos. Environ.* 41:1230–1236.

Vartiainen, E., Kulmala, M., Ruuskanen, T.M., Taipale, R., Rinne, J. and Vehkamäki, H. (2006). Formation and Growth of Indoor Air Aerosol Particles as a Result of D-

limonene Oxidation. *Atmos. Environ*. 40:7882–7892.

Wainman, T., Zhang, J., Weschler, C.J. and Lioy, P.J. (2000). Ozone and Limonene in Indoor Air: A Source of Submicron Particle Exposure. *Environ. Health Perspect.* 108: 1139–1145.

Wolkoff, P. (1999). Photocopiers and Indoor Air Pollution. *Atmos. Environ.* 33: 2129–2130.

Wolkoff, P. and Nielsen, G.D. (2001). Organic Compounds in Indoor Air – Their Relevance for Perceived Indoor Air Quality? *Atmos. Environ*. 35: 4407–4417.

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