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Ultrafine particle emissions from essential-oil-based mosquito repellent products

Abstract Ultrafine particle (UFP) emissions from three essential-oil-based mosquito repellent products (lemon eucalyptus (LE), natural insects (NI), and bite shield (BS)) were tested in a 386 l chamber at a high air exchange rate of 24/h with filtered laboratory air. Total particle number concentration and size distribution were monitored by a condensation particle counter and a scanning mobility particle sizer, respectively. UFPs were emitted from all three products under indoor relevant ozone concentrations (~ 17 ppb). LE showed a nucleation burst followed by a relatively stable and continuous emission while the other two products (NI and BS) showed episodic emissions. The estimated maximum particle emission rate varied from 5.4×10^9 to 1.2×10^{12} particles/min and was directly related to the dose of mosquito repellent used. These rates are comparable to those due to other indoor activities such as cooking and printing. The emission duration for LE lasted for 8–78 min depending on the dose applied while the emission duration for NI and BS lasted for 2–3 h.

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Practical Implications

Certain essential-oil-based mosquito repellents can produce high concentrations of UFPs when applied, even at low ozone levels. Household and personal care products that contain essential oil may need to be tested at indoor relevant ozone levels to determine their potential to increase personal UFP exposures.

Introduction

Exposure to particulate matter (PM) has been linked with increased risk of cardiovascular and respiratory diseases and an excess of mortality (Delfino et al., 2005; Pope et al., 2009). Due to their unique characteristics such as high specific surface area, ultrafine particles (UFPs, diameter < 100 nm) have higher toxic potential than larger particles with the same mass concentration (Oberdorster, 2001; Oberdorster et al., 2005; Sioutas et al., 2005). Volatile and semivolatile organic compounds (VOCs and SVOCs) emitted from household products can nucleate to form UFPs or react with ozone and form secondary organic aerosols (SOAs) (Coleman et al., 2008; Sarwar and Corsi, 2007; Sarwar et al., 2004). Studies on human activity patterns in various countries have reported that people spend most of their time in indoor environments (Brasche and Bischof, 2005; Klepeis et al., 2001; Yang et al., 2011). Therefore, it is important to identify and understand indoor UFP sources.

Scented personal care products such as lotions and perfumes are applied around the head. The VOCs emitted can form UFPs near and directly in a person's breathing zone. This creates a 'personal reactive cloud' (Corsi et al., 2007), which can be a strong source of UFP exposures. Several studies have reported particle emissions from fragrances and essential oils. A perfume was found to generate a large amount of UFPs at an ozone level of 184 ppb (Sarwar et al., 2004). In the same study, however, when an ozone level of 15 ppb was used, no significant particle emission was detected. Some essential oil fragrances used in spas were tested both in a chamber and in a spa center (Hsu et al., 2012; Huang et al., 2012). In all these tests, high concentrations of UFPs were observed. Although there are different agencies regulating fragrances, the industry is still primarily self-regulated (Bridges, 2002). For instance in the United States, the Food and Drug Administration (FDA), Environmental Protection Agency (EPA), and Consumer Products Safety Commission (CPSC) have programs for cosmetic products. These programs are either non-regulatory or not well carried out (Bridges, 2002). The International Fragrance Association (IFRA) is mainly in charge of the self-regulating process of fragrances but the guidelines of IFRA are not compulsory for manufacturers. Because neither agencies nor self-regulation of the industry provides satisfactory regulations of these products, a potential risk may exist when using these scented products including mosquito repellents.

Traditional mosquito repellent products have a large market in developing countries and tropical countries for preventing disease transmission or to simply repel pests (Liu et al., 2003). Most commonly used are incense coils, which release mosquito repelling smoke that is shown to have detrimental human health effects (Lee and Wang, 2006; Liu et al., 2003; See and Balasubramanian, 2011; See et al., 2007). Essential-oil-based mosquito repellents, which do not require burning and can be applied to a person directly, are alternatives for coils. Many of these types of mosquito repellents are claimed to be non-toxic but their potential for air pollutant emissions is poorly understood.

There are many studies focused on particle emissions from personal care and household products (Destaillats et al., 2006; Li et al., 1993; Long et al., 2000; Morawska et al., 2009a; Nazaroff and Weschler, 2004; Rossignol et al., 2013; Saathoff et al., 2009; Sarwar and Corsi, 2007; Stabile et al., 2012) or from specific ingredients used in these products (Chen and Hopke, 2010; Hoffmann et al., 1997; Northcross and Jang, 2007; Wainman et al., 2000; Weschler and Shields, 1999; Zeng et al., 2013). An important particle formation mechanism for indoor SOA is ozonolysis of VOCs and SVOCs. To account for 'worst-case' scenarios, ozone concentrations were often set at a high level (> 100 ppb) when studying indoor SOA formation. However, indoor ozone concentrations seldom reach this level. In addition, a few studies have found that certain perfumes, detergents and cleaners produced a significant amount of SOAs even at a low ozone level of ~ 20 ppb (Coleman et al., 2008; Morawska et al., 2009a; Sarwar et al., 2004). Studies have also shown that ozone generating air cleaners can form particles at low ozone levels (Hubbard et al., 2005; Waring and Siegel, 2011). In a classroom study of d-limonene ozonolysis by Morawska et al. (2009a), the threshold ozone concentration for SOA formation was found to be as low as 5 ppb. When d-limonene from cleaning products reached the highest level of 95 ppb, the particle formation rate was as high as 6×10^{12} particles/min, though the ozone concentration was only 10 ppb. Investigating UFP emissions from certain products at an indoor relevant ozone level will have more direct implications in exposure assessment.

In this study, we tested UFP emissions of three selected essential-oil-based mosquito repellents at an indoor relevant ozone level. The UFP emission patterns with different dosage were analyzed. Both peak particle concentration and total particle concentration were estimated. A new data analysis method was introduced to estimate time-resolved emission rates. Particle emissions from mosquito repellents were compared with those from other indoor activities. The potential mechanisms for particle formation are discussed.

Experimental method

Test products

Two spray-type and one cartridge-type mosquito repellents were tested for UFP emissions. These three products were all essential-oil-based. As shown in

Table 1 Summary of tested products and experimental plans

Name	Active ingredients	Notes	Tested dose (ml)	Repeated experiments
Lemon eucalyptus repel (LE)	Lemon eucalyptus	Liquid repellent for spray	0.2	7
			0.5	5
			1.0	5
			2.0	5
			5.0	5
			10.0	5
Natural insects repel (NI)	Geraniol	Liquid repellent for spray	1.0	3
Bite shield (BS)	Geraniol (carried by polyethylene pellets)	Electrical device with a fan blowing gases out	NA[a]	2

[a]Dose does not apply for this product.

Table 1, the main active ingredient of the first spray-type repellent is lemon eucalyptus (LE), which contains 30% LE oil by volume. The two major constituents of LE oil are citronellal and citronellol, which comprise 65.9% and 10.5% of the oil, respectively (Han et al., 2011). The other spray-type repellent, natural insects (NI), and the cartridge-type repellent, Bite Shield (BS), use geraniol as their active ingredient. The spray-type mosquito repellents use liquid solvents to carry the active ingredients. The cartridge-type repellent uses polyethylene pellets to carry the active ingredients. The cartridge is loaded into a miniature fan, which can be clipped to a person's belt to release the mosquito repelling vapor.

Measurements

All the experiments were conducted in a stainless steel chamber with a volume of 386 l. Filtered laboratory air was pumped into the chamber from the bottom and exhausted from the top into a fume hood. Using the CO_2 decay method (Zhang et al., 2013), the air exchange rate (AER) was estimated to be 24/h. The ventilation condition was kept the same throughout the measurements. The background particle number concentration in filtered laboratory air ranged from 200 to 1000 no./cm^3 and was subtracted from each experiment. The temperature and relative humidity in the chamber were ~ 24 ± 0.5°C and 60% ± 5%, respectively. Ozone levels in the laboratory were measured independently for several hours each day for 5 days. The average ozone concentration was 17 ± 3 ppb.

Two sample probes were set at the center of the chamber, 0.5 m above the test products, allowing simultaneous sampling using a water-based condensation particle counter (WCPC 3785, TSI, Inc., Shoreview, MN, USA) and a scanning mobility particle sizer (SMPS Model 3080, TSI, Inc., Shoreview, MN, USA). The WCPC sampled continuously at 1 s interval with a cutoff size of 5 nm. The SMPS measured particles in the size range of 7–295 nm with a scan time of 120 s (100 s of upscan and 20 s retrace). Because almost all particles were found in the ultrafine mode, only the first 80 bins of measured size distributions (7–126 nm) were used later in data analysis, which contain more than 99% of the particles in most cases.

All experimental conditions are summarized in Table 1. Prior to each experiment, the chamber was flushed for an hour with filtered laboratory air. The products were then placed in the chamber. For BS, a new battery was installed in the fan unit prior to each experiment. For NI and LE, the liquid was spread evenly on a plastic dish with a total surface area of 180 cm^2. The SMPS and CPC data were recorded until the particle concentration dropped to the background level. We sampled eight hours for BS experiments because of its episodic emission patterns. For LE, six doses (0.2, 0.5, 1, 2, 5, and 10 ml) were tested to study the effect of dose on particle formation.

Data analysis

Particle concentration

To compare different tests and products, the peak particle concentration, $C_{\max}$, and the total particle concentration, F, were used. The latter is calculated using the following equation,

$$F = \int_{t_{\mathrm{start}}}^{t_{\mathrm{end}}} \mathrm{C}\,\mathrm{d}t \qquad (1)$$

where C is the particle number concentration in the chamber minus the background concentration, no./cm^3; t_{start} and t_{end} are the start and the end time for each experiment, respectively. Similar parameters have been used previously when comparing results (Schripp et al., 2008). $C_{\max}$ indicates the extreme particle concentration level, which is important, but may be subject to high uncertainty due to specific experimental conditions. F, however, is more reliable and more relevant to exposure risk by taking both particle concentration and exposure duration into account.

Particle deposition and coagulation rate

When calculating particle loss, many previous studies have used regression of the first-order decay rate of particle concentrations (Gehin et al., 2008; He et al., 2007; Schripp et al., 2008). However, Coleman et al. (2008) pointed out that there were still particle formations during these decay periods, which will lead to an underestimation of the decay rate. The regressed particle first-order decay rate in this study was between 15 and 21/h while the AER was 24/h, which indicates a continuous emission even when particle concentration was decreasing rapidly. Therefore, instead of the regression method, particle losses due to wall deposition, coagulation, and air exchange were estimated separately in this study. Size-dependent deposition rate coefficient was calculated following Lai and Nazaroff (2000). Fuchs formula was used to calculate size-dependent coagulation rate coefficient (Seinfeld and Pandis, 2006). Using particle size distribution data from SMPS measurements, both deposition loss rate and coagulation loss rate were estimated following Coleman et al. (2008). These loss rates were then interpolated to second-by-second rates for the following emission rate estimations. Details of these calculations are given in Supporting Information.

UFP emission rate

Assuming a well-mixed chamber, the particle number balance equation can be written as,

$$\frac{dC_{\text{in}}}{dt} = \frac{E}{V} - \text{AER}(C_{\text{in}} - C_{\text{out}}) - L_{\text{dep}} - L_{\text{coag}} \qquad (2)$$

where C_{in} and C_{out} are the particle number concentration in the chamber and in the filtered laboratory air, no./cm^3, respectively. V is the chamber volume, cm^3. AER is the air exchange rate/s, L_{dep} and L_{coag} are the particle wall deposition rate and coagulation rate, no./(cm^3 s), respectively. E is the particle emission rate, no./s. To estimate E, Eq. 2 can be rearranged as,

$$E = V\left(\text{AER}(C_{\text{in}} - C_{\text{out}}) + L_{\text{dep}} + L_{\text{coag}} + \frac{dC_{\text{in}}}{\text{dt}}\right) \qquad (3)$$

where C_{in} and C_{out} were measured by the CPC. L_{dep} and L_{coag} were determined as described above. $\frac{dC_{\text{in}}}{dt}$ was calculated based on particle concentration data from the CPC. Because there were substantial noises in the CPC data (especially at high concentrations), smoothing was applied to the estimated emission rate using moving average method of 20 span. An example is shown in Figure 1, which presents particle emission, ventilation, coagulation, and deposition rates estimated for LE experiment with the dose of 0.5 ml. Using a similar method, Schripp et al. (2008) calculated time-resolved emission rates from the SMPS data. Using CPC data for concentration and SMPS data for interpolated particle deposition and coagulation loss, we improved the time resolution of particle emission rate to second-by-second. Both maximum emission rate and total emission (through integration with time) can be found from time-resolved emission rates.

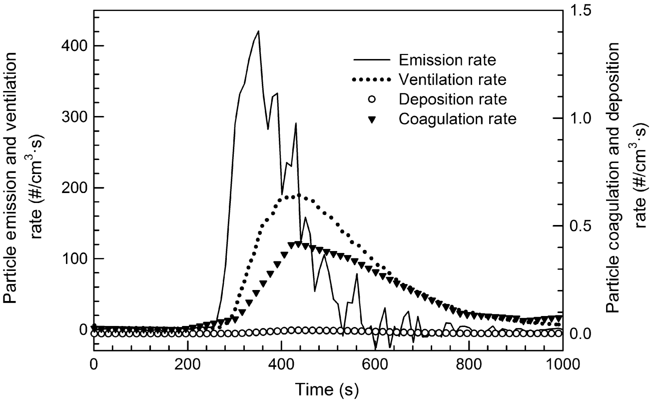

Fig. 1 Particle ventilation, deposition, coagulation, and emission rates estimated for LE experiment with the dose of 0.5 ml

Results

Particle size distribution

The size distributions of particles emitted from the three products are shown in Figure 2. Two patterns were observed. LE showed a typical initial nucleation event (Figure 2a, b). During this event, large numbers of nucleation mode particles were abruptly formed and then grew due to condensation and coagulation. When the dose of LE was high enough, a quasi-steady-state occurred following the nucleation burst (Figure 2b). The geometric mean diameter remained at ~ 30 nm and geometric standard deviation remained to be ~ 1.60. The term ‘quasi-steady-state’ refers to a state that the mode of particle size distribution is relatively stable (Coleman et al., 2008). A similar process was also observed previously (Destaillats et al., 2006). In their studies, particle emissions under ‘quasi-steady-state’ were time-independent due to the continuous addition of products. In this study, because the source was finite and particles were gradually removed by ventilation, the steady size distribution usually lasted for about 30 min.

As shown in Figure 2c, d, NI and BS were similar to each other but had a different emission pattern from LE. Their particle emissions were episodic, and pulses of UFPs were observed. Comparing to LE, UFP emissions from NI and BS lasted for a relatively longer time at a lower concentration.

Peak and total particle concentration

Figure 3 shows the peak particle concentration and total particle concentration from the LE experiments. C_{max} increases with the dose until it reaches saturation level around 2 ml. In contrast, F increases with the dose throughout the tested range. Larger variations were observed with high-dose experiments, that is, 5 ml and 10 ml. Although the applied liquid volume can be controlled precisely, other factors such as the spreading surface area and the layer thickness of LE could not be readily controlled, especially in high-dose experiments. These factors may influence the emissions to a large extent.

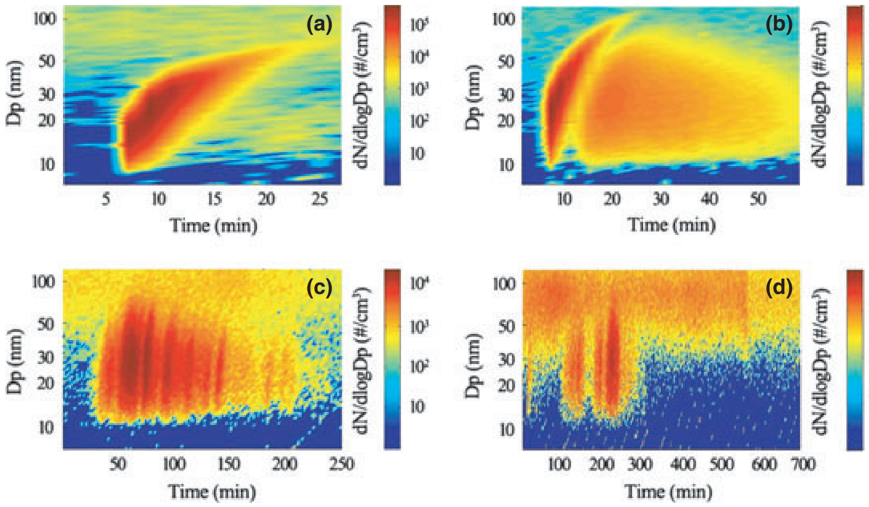

Fig. 2 Particle emission patterns for (a) LE experiment at 2 ml, (b) LE experiment at 5 ml, (c) NI experiment at 1 ml and (d) BS experiment

UFP emission rate

Table 2 summarizes particle emissions of the three tested products at different doses. Emission duration, particle ventilation sink, total particle emission, average and maximum emission rates are given. For LE, the maximum emission rate was strongly correlated with the dose applied. The average emission rates are similar to each other for LE doses of 1, 2, 5, and 10 ml. Increasing dose leads to higher maximum emission rate and also longer emission time during which low emission rate also exists. Compared with LE, NI and BS show longer emission durations and lower emission rates.

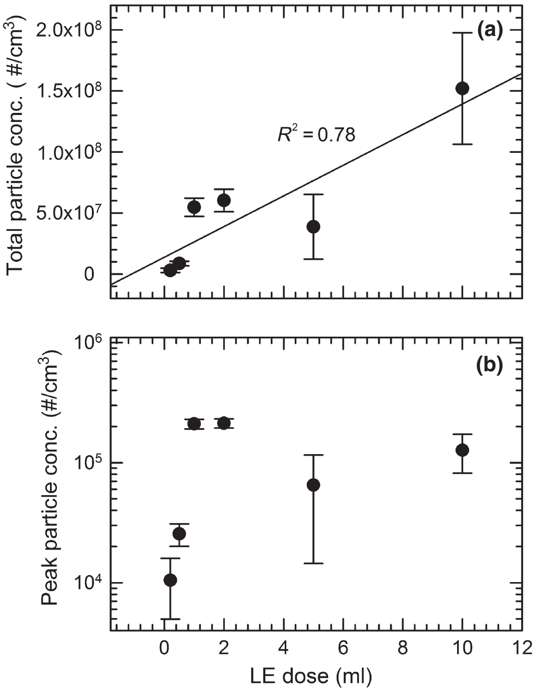

Fig. 3 (a) Total particle concentration and (b) peak particle concentration as a function of the LE dose applied

Unlike particle concentration, which is largely affected by the experimental condition such as AER, the emission rate is a more robust parameter, which allows for comparison between different products and sources. Figure 4 compares maximum emission rates from essential-oil-based mosquito repellents to those from other indoor activities reported in the literature. To be consistent with previous studies, the unit of the emission rate is converted from no./s to no./min. Both primary and secondary particle sources are given. For secondary formation, ozone levels were also included. As shown in Figure 4, although the ozone level in this study is low, the emission rates are comparable to and sometimes higher than those reported in other studies.

Discussion

Two different emission patterns were observed for the three tested mosquito repellent products. The ingredients used in these products are different. NI and BS share the same active component (geraniol) while the main ingredient in LE is citronellal (Table 1). In addition, different releasing technologies of these active ingredients may also contribute to the observed difference. The rapid dissipation of essential oil could reduce its protective effects such that different technologies were used to extend the releasing time of the mosquito repellent ingredient (Nerio et al., 2010; Trongtokit et al., 2005). For instance, inclusion complexes of citronella oil can extend the repellent protection time to 2 h (Songkro et al., 2012). The two different UFP emission profiles suggest that LE was designed as a quick releasing product while NI and BS were designed to slowly release the essential oil for hours.

Table 2 Particle emissions from three essential-oil-based mosquito repellents

Product	Tested dose (ml)	Emission duration (min)	Total particle ventilation sink ($\times 10^9$ #)	Total particle emitted ($\times 10^9$#)	Average emission rate ($\times 10^7$ no./s)	Maximum emission rate ($\times 10^7$ no./s)
LE	0.2	8.3	3.6	3.7	0.7	9.5
	0.5	8.3	18.0	18.3	3.7	44.9
	1	8.3	81.0	82.4	16.5	250.4
	2	11.7	97.3	98.4	14.1	588.5
	5	46.7	303.6	310.9	11.1	1052.8
	10	77.5	600.0	612.3	13.2	2182.9
NI	1	110.3	105.0	107.3	0.9	40.7
BS	NA[a]	210.9	149.8	150.3	1.8	45.7

[a] Dose does not apply for this product.

When particle formation and growth occur, a significant amount of gaseous precursors is consumed (Jaoui et al., 2006; Lee et al., 2006; Rossignol et al., 2013). Thus for BS and NI, the slow release of the precursors leads to their fluctuating concentration. Accordingly, particle emission patterns are episodic. For LE, the quick release of precursors leads to a nucleation burst and the following quasi-steady-state in high doses.

The gas/particle partitioning theory (Hallquist et al., 2009; Odum et al., 1996) can be used to qualitatively understand particle emissions from essential-oil-based mosquito repellent products. This theory proposes that the formation of secondary aerosol is due to the partition of low- or semivolatile organic compounds between the gas and particulate phases. Both geraniol and citronellal are terpenoids with low volatility thus presumably acting as the main partitioning species. Other low-volatile compounds might be geraniol or citronellal degradation products with more functional groups (Hallquist et al., 2009). Reactions of these two compounds with ozone, OH, and NO_3 radicals are the possible ways of degradation (Forester and Wells, 2009; Forester et al., 2007; Harrison and Ham, 2010; Harrison et al., 2007; Nunes et al., 2005). Possible pathways/products and reaction rate constants were reported. The presence of OH and NO_3 radicals in indoor environment was discussed previously (Nojgaard, 2010; Sarwar et al., 2002). Using the reported rate constants and the ozone concentration in this study, the removal rate constants due to ozonolysis were estimated to be 1.78/h for geraniol and 0.7/h for citronellal. Similarly, the removal rate constants of geraniol and citronellol by reacting with NO_3 radicals were estimated to be 1.5 and 1.1/h, respectively. Despite of the high ventilation loss rate constant (24/h), the products of these reactions should still be noticeable. Another possible contribution of the SOA formation is the heterogeneous reaction between ozone and the VOCs deposited on the chamber surface. It has been shown that the reaction probability of deposited monoterpenes are 10–100 times higher than gas-phase reaction probabilities for the same compounds (Shu and Morrison, 2011; Springs et al., 2011). The relatively high surface area to volume ratio of the chamber in this study potentially contributes to surface reactions, which then serve as a source of SOAs. A limitation in this study was that surface reaction contributions were not well accounted for and needs to be addressed in future studies. However, Waring and Siegel (2013) found only 5–10% SOA contribution from surface reactions for a typical indoor environment. Therefore, surface reaction contributions in this study were likely to be small.

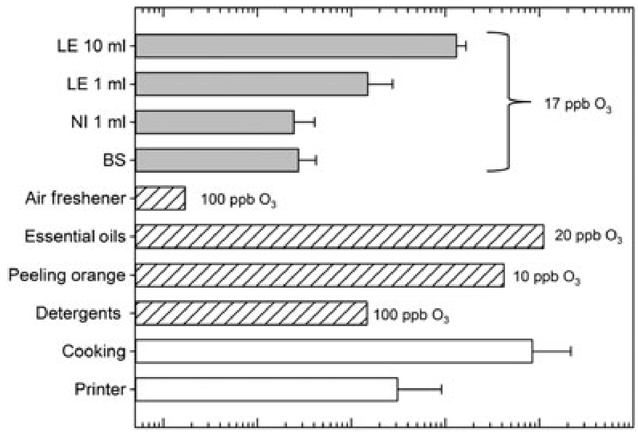

Fig. 4 Comparison of particle emission rates from the use of mosquito repellents with those from other indoor activities. The ozone levels for the secondary sources are labeled next to their corresponding bar. The literature sources are as follows: cooking (Afshari et al., 2005; Buonanno et al., 2009; Gehin et al., 2008; Glytsos et al., 2010; He et al., 2004; Wallace, 2006; Wallace et al., 2008), printers (Barthel et al., 2011; Gehin et al., 2008; Koivisto et al., 2010; Morawska et al., 2009b; Schripp et al., 2009), air freshener (Lamorena and Lee, 2008), essential oils (Hsu et al., 2012), peeling oranges (Vartiainen et al., 2006), and detergents (Morawska et al., 2009a)

Ultrafine particle emissions from different indoor sources and their source strengths were investigated previously. They include primary emission sources, such as cooking and certain electrical appliances (e.g., printers), and secondary emission sources, such as detergents and fragrant products. Cooking is considered to be a major indoor human activity for UFP emissions. Printers are another important indoor primary particle source. The average maximum emission rate is ~ 10^{13} no./min and 10^{11} no./min for cooking and printers, respectively. As shown in Figure 4, the mosquito repellents tested in this study can generate particles at a rate comparable to printers but not as high as cooking. At low ozone levels (~ 17 ppb), these repellents can generate UFP at a rate comparable to other secondary sources. To have better practical implications, indoor relevant ozone level is suggested to be used in the future indoor UFP emission studies. The settings of this study did not closely follow the practical usage of the repellent products, which could underestimate their UFP emissions. LE and NI are sprayed in practice, which might have higher precursor releasing rates than being added on a dish. In addition, the experiments were conducted at a high AER to avoid extremely high particle concentrations, which may introduce additional uncertainties. High particle concentrations can lead to dynamic changes of aerosol size distributions and high particle losses in the sampling lines. When the particle concentration is above 30,000 no./cm^3, CPC will switch from the single particle counting mode to the photometric mode, which has a lower precision. However, the high AER also reduced the concentrations of gaseous precursors. With VOCs and SVOCs ventilated out of the chamber quickly, particle formation was reduced as well. In other words, the tested products may generate more particles in a room of typical AER under common mixing processes, which deserves further study.

This study introduced a new data analysis method that combines CPC and SMPS data to estimate the emission rate with high time resolution, that is, second-by-second. To overcome the low time resolution of SMPS data (1 size distribution for every 120 s), interpolation was applied for the deposition and coagulation rates. This may lead to uncertainties in evaluating these rates. However, high AER was used in our study such that the contribution of deposition and coagulation to the total particle sink was negligible (as shown in Figure 1). Coagulation loss is proportional to the square of the particle concentration. For the highest particle concentration in our experiments, the coagulation loss rate was 30 no./(cm^3 s) comparing to the particle ventilation loss rate of 4000 no./(cm^3 s). The particle deposition rate was even lower. As shown in Table 1, therefore, total particle ventilation sinks are nearly the same to total particle emissions. Though it does not cause problems in our study, this analysis method should be adjusted properly if applied to other data with higher particle concentrations. Using a high time resolution mobility spectrometer such as a fast integrated mobility spectrometer (Kulkarni and Wang, 2006) or setting SMPS for a narrower size range and a shorter scan time may help to reduce the uncertainties.

Conclusion

We found that essential-oil-based mosquito repellent products can generate particles at low ozone levels (~ 17 ppb). Most particles generated are in the ultrafine size range. A new data analysis method was developed, which allows the estimation of time-resolved emission rates. Maximum UFP emission rates ranged from 5.4×10^9 to 1.2×10^{12} particles/min with different doses applied. The emission rates were comparable to those from other indoor sources such as cooking and printers. Two different emission patterns, continuous and episodic, were observed from the three tested products. For the LE mosquito repellent, a distinct nucleation burst was observed and followed by a relatively stable emission state if a high enough dose was applied. The emission durations varied from 8 min to 3 h. To reduce UFP exposure, we recommend applying a lower dose away from the breathing zone when using these mosquito repellent products.

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Supporting Information

Additional Supporting Information may be found in the online version of this article:

Data S1 Calculation of deposition and coagulation rate.

Reference

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