Evaluation of airborne particulate matter and volatile organic compounds released by three types of mosquito repellents

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Abstract

This study investigates the emissions from various mosquito repellents, focusing on particulate matter (PM) and volatile organic compounds (VOCs). PM was measured with a scanning mobility particle sizer (SMPS) and optical particle spectrometer (OPS) in an exposure chamber; VOCs were collected with Tenax TA and analyzed by gas chromatography–mass spectrometry. SMPS measurements in the range of 10–420 nm showed that the coil-types had the highest concentration (13,048 particles cm$^{-3}$), followed by the mat-types (119 particles cm$^{-3}$), and liquid-types (42 particles cm$^{-3}$). However, the percentage of nanoparticles was highest in the liquid-type (50%), followed by the mat (46%) and coil-types (33%) (p < 0.05). According to the OPS measurements, covering a range of 0.3–10 μm, showed the highest value for the coil-types (4,096 particles cm$^{-3}$), with similar values for the mat and liquid-types (13 particles cm$^{-3}$ each). The percentage of particles < 2.5 μm in size, which can easily enter the lower respiratory tract, was 82–99%. Coil types burn at a much faster rate (29.31 mg min$^{-1}$) than liquid (1.89 mg min$^{-1}$) and mat types (1.30 mg min$^{-1}$), indicating a more intense combustion process. Coil types also lead in emission rates (1.94 × 10$^9$ particles min$^{-1}$ for 10-420 nm) releasing more particles per minute, followed by liquid (1.87 × 10$^8$ particles min$^{-1}$) and then mat types (6.34 × 10$^7$ particles min$^{-1}$), suggesting higher particulate emissions during use. When normalized by usage weight, Coil types again show the highest emission factors (6.59 × 10$^{11}$ particles g$^{-1}$), implying they emit more particles per gram of product burned than liquid (1.82 × 10$^{11}$ particles g$^{-1}$) and mat (4.81 × 10$^{10}$ particles g$^{-1}$) types. The study highlights the need for comprehensive understanding of repellent emissions due to their potential health impacts.

Keywords: Mosquito repellent, Emission factor, Emission rate, PM, VOCs
INTRODUCTION

There are over 3,500 known species of mosquitoes worldwide and many of them are responsible for diseases such as malaria, dengue fever, plague, Japanese encephalitis, Zika virus, and yellow fever. According to the 2022 world health organization (WHO) report, an estimated 247,000,000 people were affected by malaria in 2021, with 619,000 deaths (WHO, 2022). Climate change has already begun to impact many organisms, including the populations, habitats, and associated diseases of mosquitos (Kovats et al., 2001). Extreme weather will expand the range of mosquitoes into previously unaffected areas (Bouzid et al., 2014). Rising temperatures have already increased the size and range of mosquito populations and thus the number of people infected with mosquito-borne diseases (Frankinos et al., 2019). An effective response requires a deep understanding of these changes.

Current strategies for the management of mosquito populations include eco-friendly methods such as mosquito control by the larvivorous fish Gambusia and Poecilia (Poeciliidae) (Wickramasinghe and Costa, 1986), whereas in households and similar settings mosquito repellents are the most popular control method. Following the invention of the mosquito coil in Japan in the late 19th century, various types of mosquito repellents have been developed and popularized. However, many of their ingredients are toxic, such as pyrethroids (Vesin et al., 2013; Li et al., 2016) and permethrin (Manikkam et al., 2012), with human health effects that include headaches, fatigue, and cough (Del PradoLu, 2007), as well as effects on the reproductive, endocrine, immune, and respiratory systems (Chalupka and Chalupka, 2010). Mosquito repellents also release large numbers of fine particles into the air (Löfroth et al., 1991), which may induce asthma (Kappos et al., 2004; Li et al., 2013). Studies have shown that burning a single mosquito coil emits the same amount of PM$_{2.5}$ as smoking 75 to 137 cigarettes (Liu et al., 2003). Gaseous pollutants such as polycyclic aromatic hydrocarbons...
(Zhou et al., 2009) and Volatile Organic Compounds (VOCs) (Lee and Wang, 2006; Yang et al., 2016; Zhu et al., 2018), are also released by mosquito repellents and have been shown to cause reproductive toxicity (Xia et al., 2009; Mukhopadhyay et al., 2010), neurotoxicity (Cordier et al., 1997; Niu et al., 2010; Wang et al., 2010), and cancer (Wang et al., 2017).

Consequently, insect repellents are among pesticides regulated by law in many countries. For example, in Korea, pesticides are classified as household chemicals and are subject to approval by the Ministry of Environment, such that they must undergo risk assessment conducted by the Korea Institute of Environment, Industry and Technology to confirm their compliance with safety standards. In the USA, the Federal Insecticide, Fungicide, and Rodenticide Act is enforced by the environmental protection agency (EPA), and the federal food, drug, and cosmetic act (FD&C Act) is enforced by the food and drug administration (FDA). Despite these and similar regulations in other countries, there is still a need to investigate the efficacy, resistance, environmental impact, and public health of mosquito repellents.

Many studies that have examined different aspects of mosquito control and the impact of repellents and insecticides on human health and the environment have relied on mass-based concentration measurements in their assessment of air quality affected by mosquito repellents. For example, among airborne particles, nanoparticles contribute substantially to toxicity, due to their large surface area, but they contribute little to the mass concentration; instead, they are often evaluated in terms of their number concentration (Oberdörster, 2001; Park et al., 2017; Park et al., 2020). Some studies have assessed health risks based on several methods. Sahu et al. (2013) and Wang et al. (2018) has assessed health risk using multiple-path particle dosimetry model (MPPD), Zhu et al. (2018) assessed health risk by assuming the inhalation of carbonyls based on US EPA. But fewer studies have compared different types of mosquito repellents or analyzed their particulate and gaseous substances. The purpose of this study was
to evaluate the airborne concentrations of particulate matter (PM) and VOCs resulting from
the use of mat, liquid, and coil mosquito repellents.

2 METHODS

2.1 Experimental conditions

The experiment was conducted using a non-static acrylic chamber consisting of two main
sections, a sample operating section at the front (2 m × 1 m × 1 m) and a sampling section at
the rear (1 m × 0.5 m × 0.5 m) (Fig. 1), as described in detail in previous studies (Kwon et al.,
2017; Kim and Lee, 2022). The total chamber volume, including the connection between the
two sections, is 2.5 m³. A fan (FLS600-24, Fine Powerex Co., Ltd., Gyeonggi-do, Korea)
located at the rear of the sampling section controls the flow rate within the chamber, which is
measured using a thermal anemometer (VelociCalc, 9565, TSI Inc., Shoreview, MN, USA).
An activated charcoal filter and a high efficiency particulate air (HEPA) filter are positioned
at the front end of the sample operating section and multiple HEPA filters at the rear end of
the sampling section to minimize air pollution and carryover effects.
Fig. 1. Schematic diagram of the experimental chamber.
2.2 Product selection

The repellents selected for testing were those with the highest market share in Korea, with the final selection consisting of two mat repellents (products A and B), three liquid repellents (products C, D, and E), and three coil repellents (products F, G, and H) (Table 1 and Fig. S1 and S2). Information on the components of each product was collected from the Korean Ministry of Environment (https://ecolife.me.go.kr/ecolife/) and the product labels.

Both mat mosquito repellents, product A from Korea and product B from China, had the same surface area (350 mm × 170 mm), and very similar heating sources (Fig. S2). Each mat was individually packaged and opened immediately before the experiment. All three liquid repellents were manufactured in Korea. Products C and E were produced by the same company and differed only in the presence or absence of fragrance. To minimize volatilization and emissions at room temperature, unique stoppers were employed before and after the experiment. The tests were conducted using the same heating source, manufactured by company C. Among the three coil mosquito repellents, two (products F and H) were from Malaysia and produced by the same company, differing only in their fragrance ingredients. The third was from Korea. The repellents were packaged in bulk and the packages were opened immediately before testing.
Table 1. Characteristics of the mosquito repellents used in this study. Products D and H were scented with lavender.

<table>
<thead>
<tr>
<th>Type</th>
<th>Repellent code, brand, and manufacturer</th>
<th>Country of manufacture</th>
<th>Component information</th>
<th>Product label</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mat</td>
<td>A: Fkilla, SC Johnson</td>
<td>China</td>
<td>d-cis/trans Allethrin (0.04 g)</td>
<td>d-cis/trans Allethrin, pulp plate</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Blue35-61544, butylhydroxytoluene, isopar L, piperonylbutoxide</td>
<td></td>
</tr>
<tr>
<td></td>
<td>B: Home Life, Sandokkaebi</td>
<td>South Korea</td>
<td>d,cis/trans Prallethrin (0.01 g)</td>
<td>d-cis/trans Prallethrin, butyl stearate, Linalool, citronellol, alpha amylcinnamic aldehyde</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Agent 1: butylhydroxytoluene, mat fragrance (HP-84359), 1,4-dibutyl aminoantraquinone, parasol 134, butyl stearate, piperonyl butoxide, Agent 2: butylhydroxytoluene, 1,4-dibutyl aminoantraquinone, parasol 134, butyl stearate, piperonyl butoxide, combination fragrance (HP-AG-26845)</td>
<td></td>
</tr>
<tr>
<td>Liquid</td>
<td>C: Fkilla, SC Johnson</td>
<td>South Korea</td>
<td>d,cis/prallethrin (1 g)</td>
<td>d,cis/trans Prallethrin, Exxsol D-130 (hydrotreated medium refined oil)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Acetyl tributyl citrate, butylated hydroxytoluene, Exxsol D-110, Exxsol D-130</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>D: Fkilla, SC Johnson</td>
<td>South Korea</td>
<td>d,cis/prallethrin (1 g)</td>
<td>d,cis/trans Prallethrin, Exxsol D-130 (hydrotreated medium refined oil)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Exxsol D-110, Exxsol D-130, mixed fragrance, acetyl tributyl citrate, butylated hydroxytoluene</td>
<td>Linalool, alpha- isoamylcinnamic aldehyde</td>
</tr>
<tr>
<td></td>
<td>E: Kilpapeu, Sandokkaebi</td>
<td>South Korea</td>
<td>d-trans Allethrin (2.6 g)</td>
<td>d-trans allethrin (S Biotrin), parlosol 124M, calcium propionate</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Disol 280, parasol 124M, butylhydroxytoluene</td>
<td>–</td>
</tr>
<tr>
<td>Coil</td>
<td>F: Fkilla, SC Johnson</td>
<td>Malaysia</td>
<td>d-cis/trans Allethrin (0.2 g)</td>
<td>d-cis/trans Allethrin, wood flour</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Sodium benzoate, glue powder, coconut powder, alpha starch, wood flour</td>
<td>Sodium benzoate</td>
</tr>
<tr>
<td></td>
<td>G: Kilpapeu, Sandokkaebi</td>
<td>South Korea</td>
<td>–</td>
<td>d-trans Allethrin (S Biotrin), wood flour</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Whiting</td>
<td>Calcium propionate</td>
</tr>
<tr>
<td></td>
<td>H: Fkilla, SC Johnson</td>
<td>Malaysia</td>
<td>d-cis/trans Allethrin (0.2 g)</td>
<td>d-trans Allethrin, wood flour</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Wood flour, Malcolm SJ 441394D, sodium benzoate, glue powder, coconut powder, alpha starch, methyl violet</td>
<td>Sodium benzoate, citronellol, geraniol, hydroxycitronellal</td>
</tr>
</tbody>
</table>

Main component: key substance for expressing the main functions of the product.

Subcomponents: legally designated hazardous chemicals, priority management substances, or biocidal substances.

* Information downloaded from https://ecolife.me.go.kr/ecolife/.
2.3 Sampling and analyses

The mosquito repellent was positioned at a height of 0.5 m, at 2 m from the sampling point (Fig. 1) by mounting it on a non-static acrylic pedestal. Before the start of the experiment, the product was enclosed in a polyethylene double-zipper bag and positioned above the pedestal. It was opened using a glove connected to the chamber immediately after background measurement. All tested mosquito repellents were weighed before and after use, including the burnt residual powder of the coil repellents, to calculate the burning rate (BR) and emission factor (EF). Following background measurement, the product was powered on for the mat and liquid repellents, and a lighter was used to ignite the coil repellent. If the coil repellent continued to burn brightly, it was shaken to extinguish the flame.

PM measurements were conducted using a scanning mobility particle sizer (SMPS, Nanoscan 3910, TSI Inc.) and optical particle spectrometer (OPS, model 3330, TSI Inc.) fixed at the sampling point (Fig. 1). The particle size ranges detected by the SMPS and OPS were 10–420 nm and 0.3–10 µm, respectively. Data collection was executed at 1 min intervals to ensure comprehensive monitoring. To guarantee optimal instrument performance, both the SMPS and OPS were activated 10 min prior to initiating each experimental run. The sampling point was connected to the measurement apparatus using a Tygon tube, with all junctions meticulously sealed using Parafilm to prevent any potential leaks. To ensure the accuracy and reliability of our PM measurements, we implemented the daily calibration of both the SMPS and OPS units utilizing standard calibration particles with predefined sizes and concentrations. To mitigate the influence of background noise and potential contaminants, blank tests were systematically performed before and after each experimental series. For the overlapping range of the SMPS and OPS (300–420 nm), the data were merged using multi instrument managing software (MIM™, TSI, San Jose, CA, USA), as has been performed in previous studies (Tritscher et al., 2015; Park et al., 2017). MATLAB (The Mathworks, Inc., Natick, MA, USA)
was used to visually represent real time variation in the particle count concentration based on changes in the diameter of each product over time.

VOCs were sampled using Tenax TA (stainless steel, Supelco Inc., Bellefonte, PA, USA). The flow rate at the sampling point was set to 0.1 m s\(^{-1}\), conforming to the breakthrough capacity guidelines delineated in ISO16000-9 (ISO, 2007). A low air volume pump (Gilian, LFS-113DC, Sensidyne, St. Petersburg, FL, USA) was employed to maintain a consistent sampling flow rate of 0.05 L min\(^{-1}\) over a duration of 30 min. Calibration of the pump was performed with a flowrate calibrator (Defender 510-H, Mesa Labs Inc., Lakewood, CO, USA) prior to the introduction of each new product sample. Tenax tubes containing the samples were preserved in a refrigeration unit until the time of analysis. Analytical procedures were carried out using thermo-desorption–gas chromatography–mass spectrometry (TD–GC–MS; MSD 5799B, Agilent Inc., Santa Clara, CA, USA), equipped with a capillary column (DB-624, 60 m × 0.25 mm × 1.4 µm, J&W Scientific Inc., Folsom, CA, USA) and operated in selective ion monitoring mode. To fortify the integrity and accuracy of the VOCs measurements, system suitability tests were conducted prior to the analysis of samples. Additionally, quality control samples were analyzed at regular intervals, and a method blank was run with each batch of samples to check for contamination and ensure the integrity of the analytical process. The recovery rates of known quantities of VOCs spiked into blank Tenax tubes were also measured to assess the efficiency of the sampling and analysis method. Throughout the experiment, the temperature and relative humidity inside the chamber were continuously monitored using a thermo-hygrometer (Thermo Recorder, TR-72wb, T&D Corp., Matsumoto, Japan). The temperature and relative humidity levels recorded during the sampling period were 16.2 ± 0.98 °C and 23.0 ± 2.27 %, respectively. These measurements were in accordance with the guidelines specified in ISO16000-9 (ISO, 2007).
2.4 Calculation

2.4.1 Volume and mass concentrations

The real time number concentration of particles measured by SMPS and OPS was converted into a volume concentration (μg cm\(^{-3}\)) as follows:

\[
\frac{dV}{d(\log D_p)} = \frac{\pi}{6} \times D_p^3 \times \frac{dN}{d(\log D_p)}
\] (1)

Where \(D_p\) is the diameter of the aerosol particle, and \(N\) is the number concentration. The obtained volume concentration can be further converted into a mass concentration as follows, considering an effective density of 1.5 g cm\(^{-3}\) (Khlystov et al., 2004):

\[
\frac{dM}{d(\log D_p)} = \text{effective density} \times \frac{dV}{d(\log D_p)}
\] (2)

2.4.2 Determination of BR, ER, and EF

The BR, or the rate at which a substance burns per unit time (g min\(^{-1}\)), for each pollutant or each type of mosquito repellent was calculated as follows:

\[
\text{Burning rate (BR)} = \frac{\text{weight reduction}}{\text{burning time}}
\] (3)

The concentration of hazardous substances in the air is typically expressed as the concentration per unit volume, but the data can be limited by the volume dependence of the experimental space. However, the unit commonly used for air quality standards (μg m\(^{-3}\)) represents a mass concentration that may underestimate the presence of very small particles such as PM\(_{2.5}\). Therefore, in this study, the ER was expressed as a particle number
concentration (particle min\(^{-1}\)). This metric enables a comparison of the quantity of PM generated by different products or types. The following mass balance equation was used to calculate the ER (Wang et al., 2018):

\[
Emission \ rate \ (ER) = V \left( \frac{dC_{in}}{dt} \right) + V \left( L_{dep} + L_{coag} \right) C_{in} - V \left( \frac{dC_{out}}{dt} \right) \quad (4)
\]

Where \( V \) is the volume of the chamber \( s \) (m\(^3\)), \( C_{in} \) is the concentration of pollutants within the chamber at a specific point in time (μg m\(^{-3}\)), \( C_{out} \) is the concentration of pollutants at the chamber exit at the same point in time (μg m\(^{-3}\)), \( ER \) is the rate of pollutant emission, \( L_{dep} \) and \( L_{coag} \) are the rates of particle deposition and coagulation onto the walls of the chamber, respectively (μg m\(^{-3}\) s\(^{-1}\)), \( \frac{dC_{in}}{dt} \) is the rate of change of the indoor concentration over time, \( \frac{dC_{out}}{dt} \) is the rate of change of outdoor concentration over time, \( V \left( L_{dep} + L_{coag} \right) C_{in} \) is the absorption rate due to particle wall deposition and coagulation, and \( V \left( \frac{dC_{in}}{dt} \right) \) is the increase in the indoor pollutant concentration over time.

As shown in previous studies conducted using the same dynamic chamber, PM adsorption on the chamber walls can be considered negligible (Kwon et al., 2017; Jeon et al., 2020; Kim and Lee, 2022). Consequently, the rates of wall deposition and coagulation were assumed to be zero. Furthermore, if a constant flow inside the chamber prevents the accumulation of harmful substances, resulting in insignificant changes in concentration over time, Eq. (4) can be simplified to Eq. (5), as follows:

\[
Emission \ rate \ (ER) = V \times AER \times (C_{in} - C_{out}) \quad (5)
\]
The EF, which is a metric quantifying the number of pollutants released per unit mass of material combusted, was calculated from the relationship between the BR and ER of each product. The EF is calculated as follows:

\[
Emission \, factor \, (EF) = \frac{Emission \, rate \, (ER)}{Burning \, rate \, (BR)}
\]

\[6\]

3 RESULTS AND DISCUSSION

3.1 Comparison of PM concentrations among repellent types

Table 2 summarizes the particle number concentration and mass concentration for each repellent, adjusted for the background concentration. The data represent averages of experimental values obtained from three repeated trials. All tested products exhibited elevated PM levels compared to the background concentration, with the highest emissions resulting from the coil repellent. Fig. 2 presents the real time concentration changes of particles of various sizes based on the cumulative usage time of each product. Even for products of the same type, particle generation tendencies differed. For all three repellent types, there was a consistent trend in which particles with diameters < 1 μm were most abundantly generated during product usage. However, for the mat repellents, although the heat source was the same, the size of the most highly concentrated particles differed significantly between product A (200 nm) and product B (100 nm). Among the liquid repellents, particles of 100 nm were the most prevalent, with concentrations of 120, 330, and 220 particles cm\(^{-3}\) for products C, D, and E, respectively. Among the coil repellents, there was substantial variation in both particle generation and concentration across different manufacturers. After 30 min of operation, product F produced the highest total particle number concentration (11,840 particles cm\(^{-3}\)).
whereas product G produced the highest concentration (12,080 particles cm\(^{-3}\)) after 10 min, and product H the highest concentration (6,040 particles cm\(^{-3}\)) after 45 min.

An analysis of the average concentration of particles detected by SMPS showed that the coil repellents had the highest number concentration (1,3048 ± 6346 particles cm\(^{-3}\)), which was 309 times higher than that of the mat (42.28 ± 28.88 particles cm\(^{-3}\)) and 110 times higher than that of the liquid repellents (119.10 ± 20.83 particles cm\(^{-3}\)). The concentration of the liquid repellents was 2.8 times higher than that of the mat repellents. According to the SMPS data, the percentage of nanoparticles ranged between 24 % and 51 %, with the liquid repellents having the highest percentage (49.91 ± 4.17 %,) followed by the mat repellents (45.93 ± 5.46 %) and coil repellents (32.66 ± 4.74 %); the differences were statistically significant (p < 0.05). The mass concentration of the coil repellents was highest, followed by the liquid and mat repellents, with concentrations of 366,853 ± 98,722, 2,692 ± 1,073, and 246.37 ± 27.49 µg cm\(^{-3}\), respectively. However, the highest proportion of nanoparticles with diameters < 100 nm (90 %) was determined for the liquid repellents, followed by the mat (1 %) and coil repellents (0.6 %).

The highest average number concentration as determined by OPS was measured in the coil repellents (4,095.67 ± 1,188.69 particles cm\(^{-3}\)), with similar concentrations for the mat (13.01 ± 12.08 particles cm\(^{-3}\)) and liquid repellents (13.09 ± 5.54 particles cm\(^{-3}\)). Within the measurement range of OPS (0.3–10 µm), particles with diameters ranging from 0.3 to 2.5 µm (PM\(_{2.5}\)) were proportionally dominant. The percentage of PM\(_{2.5}\) particles in all products exceeded 99.9 % based on their number concentration (Table 2), indicating that the use of mosquito insecticides is predominantly associated with ultrafine particles with diameters ≤ 2.5 µm. The mass concentration of the coil repellents was 292,088 ± 84,036 µg cm\(^{-3}\), which was 405.7 times higher than that of the liquid repellents (719.92 ± 345.04 µg cm\(^{-3}\)) and 329.7 times than that of the mat repellents (885.93 ± 682.04 µg cm\(^{-3}\)). The coil repellents produced the
highest PM$_{2.5}$ mass concentration (99 %), followed by the liquid (90 %), and mat repellents (89 %).

Fig. 3 depicts the changes in particle size and concentration over time during the use of the tested mosquito repellents. For the overlapping range of the SMPS and OPS (300-420 nm), the data were merged using MIM$^{\text{TM}}$, as has been performed in previous studies (Tritscher et al., 2015; Park et al., 2017). MATLAB was used to visually represent real time variation in the particle count concentration (by diameter) for each product over the course of the experiment. Fig. 3 shows the relationships between particle size and concentration in the air for each repellent, in terms of the cumulative duration of repellent usage. For the mat and liquid repellents, at a surface temperature of approximately 83.34 ± 1.40$^\circ$C, the concentration of particles of all diameters underwent a gradual change over the usage time, with minimal extreme differences before and after use. Conversely, for the coil repellent, with a surface temperature of 440.26 ± 42.35$^\circ$C, particles in the diameter range of 100–420 nm predominated, with abrupt fluctuations in the quantity of particles generated over time and no consistent trend.
Table 2. Particle number concentration and mass concentration of the three mosquito repellent types, based on experiments performed in triplicate.

<table>
<thead>
<tr>
<th>Type</th>
<th>Product</th>
<th>Usage (g)</th>
<th>Operating time (min)</th>
<th>dN dlogD&lt;sub&gt;p&lt;/sub&gt;&lt;sup&gt;–1&lt;/sup&gt; Particle number concentration (particles cm&lt;sup&gt;–3&lt;/sup&gt;)</th>
<th>dM dlogD&lt;sub&gt;p&lt;/sub&gt;&lt;sup&gt;–1&lt;/sup&gt; Mass concentration (µg cm&lt;sup&gt;–3&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>SMPS (10–420 nm)       Nanoparticle (≤ 100 nm)</td>
<td>OPS (0.3–10 µm)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>mean ± SD            %</td>
<td>mean ± SD</td>
</tr>
<tr>
<td>Mat</td>
<td>A</td>
<td>0.07</td>
<td>60.67</td>
<td>13.4 ± 88.89         40.47 ± 4.88</td>
<td>25.09 ± 21.58</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>0.09</td>
<td>60.67</td>
<td>71.15 ± 91.68        51.39 ± 4.82</td>
<td>0.93 ± 3.98</td>
</tr>
<tr>
<td></td>
<td>Mean</td>
<td></td>
<td></td>
<td>42.28 ± 28.88        45.93 ± 5.46</td>
<td>13.01 ± 12.08</td>
</tr>
<tr>
<td>Liquid</td>
<td>C</td>
<td>0.11</td>
<td>63.00</td>
<td>95.86 ± 86.17        53.01 ± 3.28</td>
<td>10.71 ± 2.8</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>0.09</td>
<td>61.00</td>
<td>160.66 ± 117.33      55.06 ± 4.41</td>
<td>23.65 ± 7.78</td>
</tr>
<tr>
<td></td>
<td>E</td>
<td>0.14</td>
<td>60.33</td>
<td>100.78 ± 75.42       41.66 ± 3.58</td>
<td>4.91 ± 2.93</td>
</tr>
<tr>
<td></td>
<td>Mean</td>
<td></td>
<td></td>
<td>119.10 ± 20.83       49.91 ± 4.17</td>
<td>13.09 ± 5.54</td>
</tr>
<tr>
<td>Coil</td>
<td>F</td>
<td>1.77</td>
<td>62.00</td>
<td>24,092 ± 20,055      24.45 ± 19.03</td>
<td>3.679 ± 1,931</td>
</tr>
<tr>
<td></td>
<td>G</td>
<td>1.78</td>
<td>64.00</td>
<td>2109 ± 1,697         40.87 ± 29.08</td>
<td>6.331 ± 3,524</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>1.93</td>
<td>61.33</td>
<td>12,943 ± 12,228      32.57 ± 22.59</td>
<td>2.277 ± 16,843</td>
</tr>
<tr>
<td></td>
<td>Mean</td>
<td></td>
<td></td>
<td>13,048 ± 6,346       32.66 ± 4.74</td>
<td>4.095 ± 1,188</td>
</tr>
</tbody>
</table>

D<sub>p</sub>, diameter of aerosol particles; N, number concentration of particles; OPS, optical particle spectrometer; PM<sub>2.5</sub>, particulate matter with diameter of 0.3–2.5 µm; SD, standard deviation; SMPS, scanning mobility particle sizer.
Fig. 2. Total particle number concentration according to particle size in the air before, during, and after mosquito repellent usage.

A, B: Mat repellents. C, D, and E: Liquid repellents. F, G, and H: Coil repellents. The x-axis represents particle size (10–10,000 nm), and the y-axis represents operation time (min), including a 30 min background period, followed by 60 min of product operation, and concluding with a 30 min ventilation period, for a total of 120 min. The z-axis represents the total particle number concentration, calculated as 5 min averages after merging OPS and SMPS measurements using MIM™.
Fig. 3. Changes in particle size and number concentration with operating time for each mosquito repellent type. The first 30 min are before operation, the next 60 min during operation, and the last 30 min after operation.
3.2 Comparison of BR, ER, and EF among repellent types

Table 3 summarizes the BR, ER, and EF of the tested mosquito repellents. The data were averaged from three experiments for each repellent product tested. For all measured variables, the values of the coil repellent were substantially higher than those of the mat and liquid repellents. The BR of the coil repellent was 22.6 and 5.5 times higher than those of the mat and liquid repellents, respectively. The average BR of the coil repellent (29.3 ± 2.08 mg min\(^{-1}\)) was 22.6 times higher than that of the mat repellent (1.30 ± 0.16 mg min\(^{-1}\)) and 5.5 times higher than that of the liquid repellent (1.89 ± 0.61 mg min\(^{-1}\)).

SMPS measurements of the particle number concentration and size distributions showed the highest particle ER for the coil repellent: 6.34 × 10\(^7\) ± 6.12 × 10\(^7\) particles min\(^{-1}\). This value was 306 times higher than that of the mat repellent (1.94 × 10\(^{10}\) ± 1.63 × 10\(^{10}\) particles min\(^{-1}\)) and 60 times higher than that of the liquid repellent (3.22 × 10\(^8\) ± 2.77 × 10\(^8\) particles min\(^{-1}\)). The EF followed the same trend as the BR and ER. The EF of the coil repellent (6.59 × 10\(^{11}\) ± 5.67 × 10\(^{11}\) particles g\(^{-1}\)) was 13.7 times higher than that of the mat repellent (4.81 × 10\(^{10}\) ± 4.32 × 10\(^{10}\) particles g\(^{-1}\)) and 3.6 times higher than that of the liquid repellent (1.82 × 10\(^{11}\) ± 1.42 × 10\(^{11}\) particles g\(^{-1}\)). According to the OPC measurements, the coil repellent had the highest ER (6.08 × 10\(^9\) ± 3.09 × 10\(^9\) particles min\(^{-1}\)) and the mat repellent the lowest ER (1.57 × 10\(^7\) ± 2.03 × 10\(^7\) particles min\(^{-1}\)). The trends in the EF were the same as determined in the SMPS analysis and followed the order coil > liquid > mat, as 2.10 × 10\(^{11}\) ± 1.15 × 10\(^{11}\), 1.84 × 10\(^{10}\) ± 7.52 × 10\(^9\) and 1.38 × 10\(^{10}\) ± 1.77 × 10\(^{10}\) particles g\(^{-1}\), respectively. Thus, both the SMPS and OPS analyses showed that the coil repellent had the largest BR, ER, and EF. These findings unequivocally demonstrate that the coil repellent generates significantly larger amounts of PM for the same quantity of repellent.
The data suggests that coil products, likely due to their higher usage weight and operating time, have much higher emission rates and factors, making them potentially more impactful in terms of particulate emissions.

The distinction between SMPS and OPS size ranges in the emission data highlights the importance of considering particle size when evaluating emissions, as different products have different emission profiles depending on the particle size range.

There is considerable variability within and between product categories, particularly in emission rates and factors, indicating that product composition and form factor significantly influence these parameters.

To comprehend these variations, it is imperative to consider the composition and combustion mechanisms inherent to each type of repellent. Coil repellents typically incorporate a higher concentration of active ingredients and combustible materials, thereby contributing to elevated burning rate (BR), emission rate (ER), and emission factor (EF). The distinctive physical structure of coils, facilitating a continuous and slow burn, also plays a pivotal role in the observed heightened emission profiles. In contrast, mat and liquid repellents are engineered for controlled vapor release, often achieved through electric heating, resulting in diminished BR and, consequently, lower ER and EF. The formulation of these repellents, typically comprising a blend of volatile substances with a reduced proportion of solid combustible materials compared to coils, further elucidates their comparatively lower emission values. An understanding of these material and design distinctions is indispensable for interpreting the discernible variations in BR, ER, and EF among the mosquito repellent types.
Table 3. Burning rate, emission rate, and emission factor data (means ± SD).

<table>
<thead>
<tr>
<th>Type</th>
<th>Product</th>
<th>Usage (g)</th>
<th>Operating time (min)</th>
<th>Burning rate (mg min(^{-1}))</th>
<th>Emission rate (particles min(^{-1}))</th>
<th>Emission factor (particles g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>SMPS (10–420 nm)</td>
<td>OPS (0.3–10 (\mu)m)</td>
</tr>
<tr>
<td>Mat</td>
<td>A</td>
<td>0.07</td>
<td>60.67</td>
<td>1.16 ± 0.017</td>
<td>2.01 × 10(^7) ± 2.69 × 10(^7)</td>
<td>1.76 × 10(^{10}) ± 2.32 × 10(^{10})</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>0.09</td>
<td>60.67</td>
<td>1.44 ± 0.059</td>
<td>1.07 × 10(^8) ± 2.95 × 10(^8)</td>
<td>7.87 × 10(^{10}) ± 2.11 × 10(^{11})</td>
</tr>
<tr>
<td></td>
<td>Sub mean</td>
<td></td>
<td></td>
<td>1.30 ± 0.16</td>
<td>6.34 × 10(^7) ± 6.12 × 10(^7)</td>
<td>4.81 × 10(^{10}) ± 4.32 × 10(^{10})</td>
</tr>
<tr>
<td>Liquid</td>
<td>C</td>
<td>0.11</td>
<td>63.00</td>
<td>1.79 ± 0.033</td>
<td>1.39 × 10(^8) ± 3.03 × 10(^7)</td>
<td>7.87 × 10(^{10}) ± 1.96 × 10(^{10})</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>0.09</td>
<td>61.00</td>
<td>1.49 ± 0.053</td>
<td>1.87 × 10(^8) ± 3.99 × 10(^8)</td>
<td>1.22 × 10(^{11}) ± 2.63 × 10(^{11})</td>
</tr>
<tr>
<td></td>
<td>E</td>
<td>0.14</td>
<td>60.33</td>
<td>2.39 ± 0.87</td>
<td>6.41 × 10(^8) ± 5.55 × 10(^8)</td>
<td>3.44 × 10(^{11}) ± 5.34 × 10(^{11})</td>
</tr>
<tr>
<td></td>
<td>Sub mean</td>
<td></td>
<td></td>
<td>1.89 ± 0.61</td>
<td>3.22 × 10(^8) ± 2.77 × 10(^8)</td>
<td>1.82 × 10(^{11}) ± 1.42 × 10(^{11})</td>
</tr>
<tr>
<td>Coil</td>
<td>F</td>
<td>1.77</td>
<td>662.00</td>
<td>28.62 ± 0.27</td>
<td>3.57 × 10(^{10}) ± 1.85 × 10(^{10})</td>
<td>1.24 × 10(^{12}) ± 6.38 × 10(^{11})</td>
</tr>
<tr>
<td></td>
<td>G</td>
<td>1.78</td>
<td>64.00</td>
<td>27.76 ± 2.02</td>
<td>3.16 × 10(^{10}) ± 1.58 × 10(^{10})</td>
<td>1.12 × 10(^{11}) ± 5.01 × 10(^{10})</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>1.93</td>
<td>61.33</td>
<td>31.55 ± 1.15</td>
<td>1.94 × 10(^{10}) ± 6.74 × 10(^{9})</td>
<td>6.21 × 10(^{11}) ± 2.38 × 10(^{11})</td>
</tr>
<tr>
<td></td>
<td>Sub mean</td>
<td></td>
<td></td>
<td>29.31 ± 2.08</td>
<td>1.94 × 10(^{10}) ± 1.63 × 10(^{10})</td>
<td>6.59 × 10(^{11}) ± 5.67 × 10(^{11})</td>
</tr>
</tbody>
</table>

Each product was tested in triplicate.
Fig. 4. Comparison of burning rate (left), emission rate (middle), and emission factor (right) among mosquito repellent types.
3.3 Comparison of VOCs concentrations among repellent types

Table 4 summarizes the 16 VOCs consistently detected among the 23 components quantitatively analyzed in the preliminary study. The detection limits are presented in Table S3. The average VOCs concentrations measured in this study were similar between solid and liquid forms, whereas the differences between the mat and coil repellents and between the liquid and coil repellents were significant.

As EPA defined limits for benzene, toluene, ethylbenzene, and xylene (BTEX) are 16 µg m$^{-3}$ (5 ppb), 3,896.87 µg m$^{-3}$ (1 ppm), 3,143.08 µg m$^{-3}$ (0.7 ppm), and 44,898.13 µg m$^{-3}$ (10 ppm). In our study, BTEX concentrations were below these standards. For all three repellent types, the concentrations of n-hexane, ethyl acetate, and toluene were higher than those of the other constituents. Nonetheless, n-hexane, the most frequently detected substance, showed notable concentration disparities between repellent types, with a 2.4- and 2.05-fold higher concentration than the mat and liquid repellents, respectively. The coil repellent also had the highest concentrations of d-limonene, octane, and styrene. As shown in the previous study that oxygen content of the repellent is the key determinant of emission factor of VOCs (Yang et al., 2016), the difference of most frequently detected substance by the types may due to the difference in chemical composition.

The TVOC content of the coil repellent was also the highest, followed by the liquid and mat repellents. The higher the atomic hydrogen/carbon (H/C) ratio, the higher the TVOC emissions. If repellents have similar H/C ratios and lower oxygen and carbon contents, it contains greater amount of heteroatoms and CaCO$_3$. This could lead to the consumption of hydrogens and reduce the possibility for the formation of CHCH fragments, which is available for VOCs formation during smoldering (Yang et al., 2007). Although in this study, H/C ratio and oxygen content are not measured, additional measurements of H/C ratio and oxygen content in further
studies may provide a clearer picture of the TVOCs in different types of mosquito repellents and why different types of VOCs occur.

Ventilation significantly reduces TVOC and formaldehyde concentrations (Salvi et al., 2016; Wang et al., 2018) as well as PM concentrations, and may therefore reduce the health risk associated with the use mosquito repellents. Notably, the very high ER and VOCs concentration associated with coil repellents suggests a need for frequent ventilation and outdoor use. The VOCs analysis targeted 16 substances for which acute toxicity data are available and chemical exposure and regulatory standards have been issued by the EPA and ACGIH. All 16 VOCs are acutely hazardous with respect to airborne respiratory exposure, inhalation hazard, respiratory absorption potential, and respiratory sensitization. Previous studies have shown that, similar to other household products (Kemmlein et al., 2003; Wilke et al., 2004; Katsoyiannis et al., 2006; Kwon et al., 2007), 3D printer operation (Kim et al., 2015) emits a variety of VOCs, some of which were also emitted from the mosquito repellents tested in this study.

The coil repellents had the highest overall VOCs concentrations, with a variety of VOCs detected across all tested brands. Unlike a previous study which reported that the VOCs with the highest detected concentrations were benzene, methylene chloride, and toluene (Lee and Wang, 2006), in our study, the VOCs with the highest detected concentrations for all tested repellents were n-hexane, ethyl acetate, and toluene. The difference might be attributed to the variations in coil chemical composition or different experimental conditions.
Table 4. Average concentrations of VOCs emitted by three mosquito repellent types (ng m\(^{-3}\)).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mat (N = 2)</th>
<th>Liquid (N = 3)</th>
<th>Coil (N = 1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>0.140 ± 0.044</td>
<td>0.084 ± 0.020</td>
<td>0.128 ± 0.021</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>0.064 ± 0.046</td>
<td>0.090 ± 0.031</td>
<td>0.133 ± 0.033</td>
</tr>
<tr>
<td>Cyclohexane, methyl-</td>
<td>0.044 ± 0.027</td>
<td>0.099 ± 0.075</td>
<td>0.108 ± 0.033</td>
</tr>
<tr>
<td>D-Limonene</td>
<td>0.051 ± 0.042</td>
<td>0.031 ± 0.013</td>
<td>0.018 ± 0.006</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>0.290 ± 0.097</td>
<td>0.870 ± 0.749</td>
<td>1.150 ± 0.230</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>0.059 ± 0.016</td>
<td>0.105 ± 0.089</td>
<td>0.146 ± 0.043</td>
</tr>
<tr>
<td>Heptane</td>
<td>0.083 ± 0.012</td>
<td>0.142 ± 0.049</td>
<td>0.157 ± 0.037</td>
</tr>
<tr>
<td>Isopropyl benzene</td>
<td>0.002 ± 0.000</td>
<td>0.002 ± 0.001</td>
<td>0.003 ± 0.000</td>
</tr>
<tr>
<td>Methyl isobutyl ketone</td>
<td>0.040 ± 0.005</td>
<td>0.045 ± 0.014</td>
<td>0.062 ± 0.012</td>
</tr>
<tr>
<td>Nonane</td>
<td>0.021 ± 0.002</td>
<td>0.043 ± 0.011</td>
<td>0.053 ± 0.006</td>
</tr>
<tr>
<td>Octane</td>
<td>0.037 ± 0.009</td>
<td>0.069 ± 0.049</td>
<td>0.067 ± 0.016</td>
</tr>
<tr>
<td>Styrene</td>
<td>0.011 ± 0.004</td>
<td>0.069 ± 0.131</td>
<td>0.023 ± 0.010</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.333 ± 0.152</td>
<td>0.523 ± 0.414</td>
<td>1.103 ± 0.332</td>
</tr>
<tr>
<td>Xylene</td>
<td>0.070 ± 0.021</td>
<td>0.100 ± 0.053</td>
<td>0.165 ± 0.033</td>
</tr>
<tr>
<td>α-Methyl styrene</td>
<td>0.004 ± 0.004</td>
<td>0.003 ± 0.001</td>
<td>0.003 ± 0.000</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>5.350 ± 5.082</td>
<td>6.279 ± 11.989</td>
<td>12.874 ± 3.325</td>
</tr>
<tr>
<td>TVOC</td>
<td>1.330 ± 0.753</td>
<td>3.314 ± 1.920</td>
<td>4.335 ± 0.247</td>
</tr>
</tbody>
</table>

Each product was tested in triplicate.

N, number of products.
To evaluate the health risks of mosquito repellents, standardized testing protocols should be established for consistent and comparable emission analyses, focusing on particulate matter (PM) and volatile organic compounds (VOCs) across different product types (coil, mat, liquid). Emphasis should be placed on particle size distribution, especially nanoparticles and fine particles, due to their potential to penetrate deep into the respiratory tract. Comprehensive studies including controlled chamber studies, real-world exposure monitoring, toxicological testing, and epidemiological research are crucial. These should be complemented with emission rate and factor calculations, alongside risk assessment models, to characterize the intensity of emissions and their health implications. This integrated approach, combining analytical techniques and health risk assessments, will provide a clearer understanding of the potential health impacts of various mosquito repellents and guide safer consumer choices.

A limitation of this study was that the experiments were conducted in a chamber rather than in an environment that simulates a residential environment, such as a real room (Lu et al., 2020) or standard apartment sized bedroom recreated in a laboratory (Li et al., 2016). However, chamber studies allow the control of variables other than the characteristics of each product, as well as objective measurements of the ER, BR, and EF of each product. To minimize the possibility of under- or overestimation due to adsorption and contamination of emissions, the chamber used in our study was washed with a detergent solution, rinsed with distilled water, dried, and purged before and after each test. Additionally, the temperature and humidity of the dynamic chamber were held constant and a HEPA filter and activated charcoal filter were used to reduce the effects of background contaminants.

4 CONCLUSIONS
This study evaluated the emissions and airborne concentrations of the PM and VOCs released from several types of mosquito repellents.

The study's findings highlight significant differences in the emission profiles of various mosquito repellent types, with coil types demonstrating notably higher particulate matter (PM) concentrations, faster burning rates, and greater emission rates compared to liquid and mat types. Notably, coil repellents not only emitted the highest quantity of particles but also had a larger fraction of smaller particles, which are of particular concern due to their potential to penetrate deep into the respiratory tract. Despite liquid types having a lower overall particle concentration, they contained the highest percentage of nanoparticles, suggesting that even lower-emitting repellents can pose health risks due to the deep lung penetration of these fine particles. The data underscores the importance of considering both the physical form and chemical composition of repellents in evaluating their health impacts, pointing to the need for comprehensive regulatory standards that address the wide range of emissions and their potential health effects. This study clearly indicates that while all repellent types contribute to indoor air pollution, coil types are particularly concerning and warrant closer scrutiny and potential reevaluation of their safety for widespread use.

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DISCLAIMER
The authors have no conflicts of interest to report.
REFERENCES


