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Effects of device type and liquid composition on characteristics of aerosols generated from tank-style e-cigarette and JUUL pod

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Effects of device type and liquid composition

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A thesis submitted in partial satisfaction

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by

Yuening Guo

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ABSTRACT OF THE THESIS

Effects of device type and liquid composition

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by

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Master of Science in Environmental Health Sciences

University of California, Los Angeles, 2021

Professor Yifang Zhu, Chair

E-cigarettes (E-cigs) experienced its unprecedented popularity over the past ten years, especially among adolescents. Tank devices and JUUL pods are the newest and most widely-used e-cigarette devices. However, there are substantial differences between their device structures and e-liquid compositions. The characteristics of aerosols generated from these two devices warrant better understanding and cross-comparisons for future human exposure studies and policymaking. This work compared the relative effect of device type (Vapor-fi Volt II tank device vs. JUUL pods) and type of nicotine used in e-liquids (freebase nicotine vs. nicotine benzoate salt) on the characteristics of mainstream e-cigarette aerosols under one and three 4-

second puffs. The e-cigarette aerosol was introduced into a 460-L mixing chamber and then measured for particle number concentration (PNC), $PM_{2.5}$ mass concentration, size distribution, and evaporative properties (i.e., particle lifetime and volatility). All measurements were taken in both puffing levels. The results suggested similar PNC levels between tank and JUUL devices. Nevertheless, JUUL generated more than twice of ultrafine particles (diameter < 0.1 μm) than tank devices. $PM_{2.5}$ from tank device were more than two times higher than from the JUUL. Device type was a significant indicator for $PM_{2.5}$ ($p < 0.05$) but not for PNC. Bimodal size distribution was observed in all samples, with the first mode at 0.06-0.09 μm and second mode at 0.27-0.31 μm. Nicotine type was only a significant indicator for PNC in 1-puff samples, and it had almost no effect on $PM_{2.5}$. Aerosols generated from tank devices were significantly less volatile than JUUL ($p < 0.05$), while volatility for the two nicotine types has no significant difference. Overall, device type had more substantial effects on aerosol characteristics than nicotine types in e-liquids. Future studies on e-cigarette exposures should consider treating tank devices and JUUL pods as two distinct emission sources.

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1. Introduction:

E-cigarettes (e-cigs) are battery-powered nicotine delivery devices that were initially introduced as an alternative to tobacco cigarettes, and were also advertised as smoking cessation aids (Glantz & Bareham, 2018; Li et al., 2019). It was introduced in the mid-2000s, but had its popularity increased among adolescents in recent years, especially after 2015 (Huang et al., 2019; McKelvey et al., 2018). Multiple generations of e-cig products, including disposable "cigalike" devices (first generation), prefilled cartridge devices (second generation), sub-ohm tank-style devices (third generation), and pod devices (fourth generation), were developed since its initial introduction. Device portability and user experience were significantly improved in the third and fourth-generation devices (Glantz & Bareham, 2018; Mathur & Dempsey, 2018). Tank devices became popular in the last five years for their high customizability and unique sensational experience upon vaping. Pod devices, especially JUUL, took over the market by their sleek design, variety of flavors, and well-designed advertisements (Dai & Hao, 2020; Huang et al., 2019).

Typical e-cig devices contain a battery to power a built-in heating element (the "atomizer") through the control of pushbuttons or air pressure sensors located in the device. The heating element is in contact with the "e-liquid," which is stored in refillable cartridges or pre-packed pods. When powered, the heating element aerosolizes the e-liquid and generates aerosol for user inhalation. E-liquids are usually liquid mixtures that contain propylene glycol (PG), vegetable glycerin (VG), nicotine, and sometimes flavoring chemicals. The first three generations of e-cig devices used freebase nicotine in their e-liquids. In contrast, the pod devices introduced nicotine salt as their new nicotine source for a higher nicotine delivery dose and less irritation to users' throats (Goniewicz et al., 2019; Talih et al., 2019). Different generations of e-cigs share the "battery + heating element + e-liquid cartridge/pod" structure. Still, they vary substantially in the setup of the heating element and e-liquid tank, mechanical structure connecting different elements, and the control and customizability of power source (Mathur & Dempsey, 2018; McKelvey et al., 2018; Protano et al., 2018).

The particle characteristics of e-cig aerosols are fundamental parameters for assessing their human respiratory exposures and potential health impacts. For e-cig aerosols, particle level and size distribution were related to the device type, chemical compositions of the e-liquids, the exhalation pattern by the user, and indoor environmental factors (El-Hellani et al., 2018; Li et al., 2019, 2020). E-cig devices of the first three generations were extensively studied for their aerosol properties; The results suggested that mainstream e-cig aerosols contain a majority of sub-micrometer-ranged ($d_p < 1$ μm) particles, usually with a bimodal distribution (Ingebrethsen et al., 2012; Melstrom et al., 2017; Oldham et al., 2018; Soule et al., 2017; Volesky et al., 2018; Zhao et al., 2017). Compared to e-cigs of previous generations, sub-ohm tank-style e-cigs (third-generation) operate at a higher voltage and may release higher $PM_{2.5}$ concentrations (Talih et al., 2015, 2017). The PG/VG/nicotine ratio of e-liquids affects PNC and $PM_{2.5}$ mass concentration in tank devices (Li et al., 2020). Pod devices (fourth generation), especially JUUL, were reported to produce much higher PM_1 (particulate matter with aerodynamic diameter less than 1 μm) and nicotine concentrations than the first three generations of devices, posting potential health concerns (Protano et al., 2018; Reilly et al., 2019; Talih et al., 2019). High variability of PM concentration and atmospheric carbonyl concentration was also observed in the same pod device with different e-liquids (Oldham et al., 2021; Protano et al., 2020). As tank and pod devices are both different in their design and e-liquid compositions in the cartridge, it remains unclear which factor contributes more to the variability in particle level and size distributions. There is a research need to evaluate the particle level and size distributions of JUUL aerosols and comparing the relative effect of device type and e-liquid composition on these characteristics.

The presented study aimed to compare the relative effect of device type and the type of nicotine used in e-liquids (freebase nicotine vs. nicotine benzoate salt) on the characteristics of mainstream e-cigarette aerosols. Vapor-fi Volt II sub-ohm tank device and JUUL pods were selected as representative tank and pod devices in this study based on their popularities among users (Baweja et al., 2016; Dai & Hao, 2020). The comparison was made under two puffing levels, i.e., one and three 4-second puffs, to observe potential variations in particle characteristics, including particle number concentration (PNC), $PM_{2.5}$ mass concentration, particle size distribution, and evaporative properties (i.e., particle lifetime and volatility).

2. Methods:

2.1 Experimental Setup

The sampling system was used in several previous studies (Li et al., 2020; Luo et al., 2021; Zhao et al., 2017). It is consisted of a high efficiency particulate air (HEPA) filter capsule that filtered the particles in the inlet air, an e-cig puffing device with adjustable puffing topography, a 460 L stainless steel chamber for aerosol solution and mixing, and the sampling instruments that were connected at the outlet of the chamber (See Figure 1).

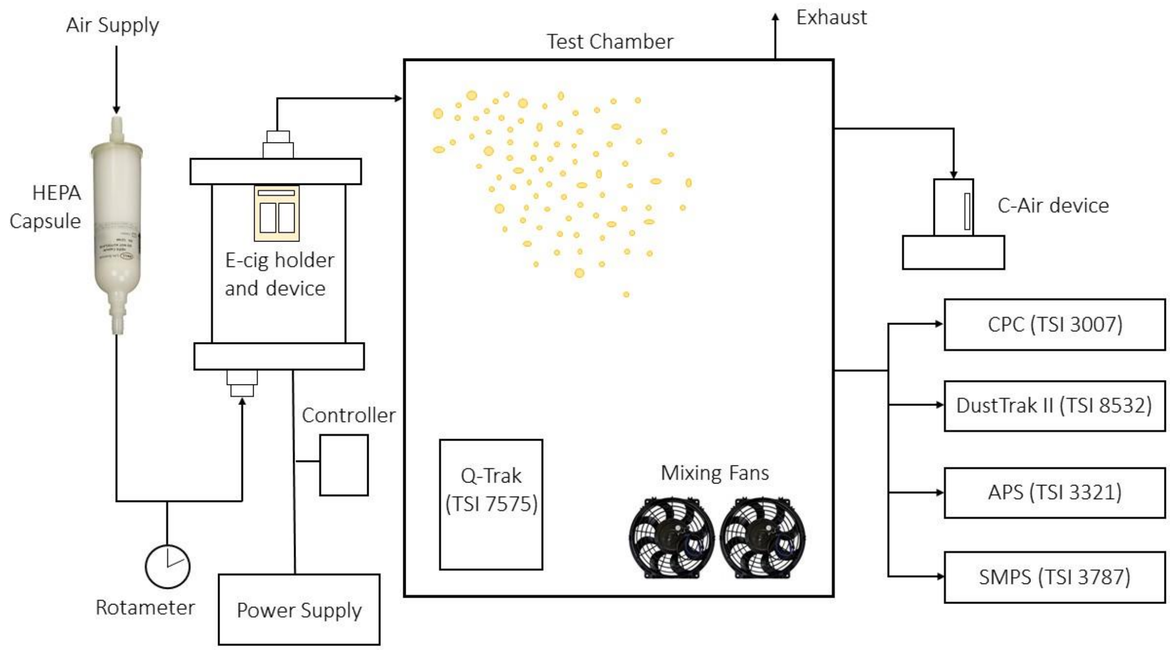


Figure 1. Schematic diagram of the aerosol generation, mixing, and sampling system

The e-cig puffing device was composed of an acrylic holder that was adjustable to JUUL and tank devices, a power source, and an Arduino UNO R3 microcontroller. According to the user manual of both devices, JUUL devices were powered at 3.7 V and 2.5 A; The Vapor-fi Volt II Hybrid Tank (as "tank device" below) was equipped with a 0.5-ohm heating coil and powered at 7.5 V and 2.5 A.

The air exchange rate of the chamber was maintained at 1 h^{-1}, meaning that the air inside the chamber was replaced once every hour. Two mixing fans were operating inside the chamber to ensure adequate air mixing and dilution. Temperature and humidity were kept at 24 ± 2°C and 25% ± 5%, and were monitored by an indoor air quality monitor (Q-Trak 7575, TSI Inc.) inside the test chamber. The dilution ratio of the chamber was approximately 6900:1(Li et al., 2020).

There were several instruments connecting at the outlet of chamber to measure PNC, $PM_{2.5}$ concentration, particle size distribution, and volatility. A portable Condensation Particle Counter (CPC 3007, TSI Inc.) was used to measure PNC. An Aerosol Monitor (DustTrak II 8532, TSI Inc.) was used to measure the $PM_{2.5}$ mass concentration. Before each sampling session, the background PNC and $PM_{2.5}$ inside the chamber was kept at < 100 particles/cm^3 and < 0.1 μg/m^3, respectively. A Scanning Mobility Particle Sizer (SMPS 3080 connecting to a CPC 3787, TSI Inc.) was used to measure the particle size distribution from 0.01 μm to 0.5 μm. An Aerodynamic Particle Sizer (APS 3321, TSI Inc.) was used to measure size distribution from 0.5 μm to 19.8 μm. The $PM_{2.5}$ data measured by DustTrak II 8532 were calibrated using gravimetric methods in previous studies, and a calibration factor of 0.27 was applied here (Nguyen et al., 2019; Zhao et al., 2017). The measurement of particle lifetime and volatility, including the description of the c-Air device, is introduced in section 2.5.

2.2 Preparation of e-liquids and puffing topography

Two kinds of nicotine - freebase nicotine and nicotine benzoate salt - were used in the e-liquids to compare the characteristic difference of the generated particles. Nicotine benzoate salt (as "nicotine salt" below) was made from mixing pure nicotine and benzoic acid at a mass ratio of 5:4. The mixture was heated at 55°C for 20 minutes until the two chemicals were completely dissolved and formed an orange oily mixture (Bowen et al., 2015). In e-liquids with nicotine benzoate salt, the nicotine equivalent concentration was equal to the mass of pure nicotine that were added in the mixture, which was approximately 5/9 of the mass of the nicotine-benzoic acid mixture. For e-liquids with both kinds of nicotine, the PG/VG volumetric ratio was set at 30/70, and the level of nicotine was set at 3% (by mass) to resemble the liquid used in JUUL and its tank counterparts on the market (Talih et al., 2019). Chemicals used in e-liquids, including PG ($C_3H_8O_2$, ≥99.5% purity), VG ($C_3H_8O_3$, ≥99.5% purity), nicotine ($C_{10}H_{14}N_2$, ≥99% purity), and benzoic acid ($C_7H_6O_2$, ≥99% purity), were purchased from Sigma-Aldrich. All the e-liquids were well-mixed and prepared within 7 days before each experiment. Liquids with nicotine benzoate salt were stored in dark and refrigerated places during the whole course of the experiment. Original JUUL pods were emptied and cleaned before filling e-liquids. E-liquid containers for both JUUL and tank devices were cleaned with isopropyl alcohol before use.

The puffing topography followed the protocol of previous studies (Li et al., 2020; Luo et al., 2021; Zhao et al., 2017). In order to mimic natural human puffing behavior, the flow rate of air flowing in the e-cig device was maintained at 1 L/min. The generation of e-cig aerosol followed a 30-second puffing cycle, with the first 4 seconds puffing and the next 26 seconds resting (Behar et al., 2015; Farsalinos et al., 2013; Robinson et al., 2015). Consequently, for the two puffing levels – 1 and 3 e-cig puffing cycles, the total puffing duration was 30 seconds and 90 seconds, respectively. The PNC and $PM_{2.5}$ concentrations were measured at the end of the puffing session. For every experimental condition, at least three replications were done to minimize the effect of random error. For the average values of PNC, $PM_{2.5}$, and particle number concentrations in each size bin, 33 observations for each variable were used for the calculations reported in sections 3.1 and 3.2.

2.3 Linear mixed-effects models

To compare the relative magnitude of effects between e-cig device and nicotine type on the variations in PNC and $PM_{2.5}$ concentrations, linear mixed-effects models were used to analyze the PNC and $PM_{2.5}$ data. The fixed-effects X variables include device type ("Device") and nicotine type ("Nic"), with both variables binarily coded. For device type, 0 and 1 represent JUUL device and Tank device, correspondingly. While for nicotine type, 0 and 1 stand for pure nicotine and nicotine benzoate salt. An interaction term between the two fixed-effects X variables was also added into the model. PNC and $PM_{2.5}$ were considered as dependent variables. To better account for the temporal autocorrelation between experiments, sampling dates of the data were coded as a random-effects variable in the model. The two emission levels (1 puff vs. 3 puffs) were separately analyzed (See Table 3). Same as , a total of 33 observations were used to fit the model.

The linear mixed-effects model of PNC and $PM_{2.5}$ were expressed as follows:

$$PNC_i = \beta_{PNC,0} + \beta_{PNC,1}Device_i + \beta_{PNC,2}Nic_i + \beta_{PNC,3}Device_i \cdot Nic_i + u_i + \epsilon_i \quad (1a)$$

$$PM_{2.5_i} = \beta_{PM_{2.5},0} + \beta_{PM_{2.5},1}Device_i + \beta_{PM_{2.5},2}Nic_i + \beta_{PM_{2.5},3}Device_i \cdot Nic_i + u_i + \epsilon_i \quad (1b)$$

Where:

- PNC_i and $PM_{2.5_i}$ are the PNC and $PM_{2.5}$ concentrations of the ith observation.
- $\beta_{PNC,0}, \dots, \beta_{PNC,3}$ are fixed-effects coefficients for PNC, while $\beta_{PM_{2.5},0}, \dots, \beta_{PM_{2.5},3}$ are fixed-effects coefficients for $PM_{2.5}$.
- $Device_i$ and Nic_i are dummy variables indicating device types and nicotine types in the e-liquids in the ith observation.

- b_{PNC} and $b_{PM_{2.5}}$ are random-effect coefficients for PNC and $PM_{2.5}$, respectively.
- u_i denotes the random-effects term, being correlated to the sampling date for observation i. The variable was coded directly in Date form to account for potential temporal autocorrelations.
- ϵ_i is the random error for observation i. The errors in the observations are assumed to be multivariately normally distributed. The models were conducted using R 4.0.5 with "nlme" package (Pinheiro, 2021).

2.4 Particle lifetime and volatility measurements

Volatility, or "rate of evaporation", is used to describe the rate of change of particle size over time. In modeling approaches for particle volatilities, the sessile droplet technique was widely used in previous studies (van der Heijden et al., 2018). Droplets were assumed to be spherical caps positioned on a substrate surface. Measurements of contact angle between the droplet edge and the substrate (θ), contact base diameter (W), drop spherical radius (r), and drop height (h) can be used to describe the change in particle size (Fang et al., 2005) (see Figure 3). Particle evaporation is a complex multi-stage process in which three to four evaporation modes with different particle shape features were developed over time (Shanahan & Bourgès, 1994). For example, for water droplets, the modes of evaporation shifted from a "pinned" mode (constant contact base diameter, decreasing contact angle) to a "receding" (constant contact angle, decreasing contact base diameter) mode after ~550 seconds (van der Heijden et al., 2018). With the full evaporation process undergoing in less than a minute, e-cig aerosols are likely to have their evaporation process in the "pinned" mode (Davies et al., 2012; Li et al., 2020; Schripp et al., 2013). Therefore, in this study, volatility of e-cig aerosols is defined as the decay rate of the contact angle [$\theta(t)$] between the droplet edge and the substrate.

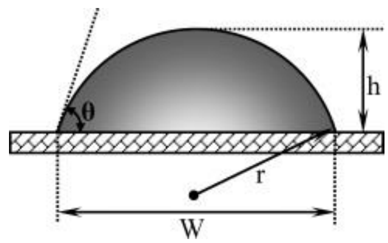


Figure 2. Schematic drawing of a sessile droplet, with definitions of contact angle (θ), contact base diameter (W), drop spherical radius (r), and drop height (h). From Fang et al. (2005).

Previously, the c-Air device was used to measure aerosol particle lifetime and volatility for tank devices (Luo et al., 2021). This study expanded the use of the device into JUUL aerosols. The c-Air device is an impactor-based mobile imaging device that captures the inline hologram of particles greater than 1 μm diameter, at 2 frames per second. The sequential holographic images of individual particles were processed using a deep-learning-based algorithm, revealing changes of the particles at 0.5-second time intervals during their evaporation. The lifetime of individual particles was defined as the time between the particle's initial landing and its complete disappearance on the impactor surface. The volatility (i.e., the contact angle decay rate K_i [in rad/s]) of every individual particle i was fitted using a linear model. i.e.,

$$\theta_i(t) = \theta_{i0} - K_i \cdot t \qquad (2)$$

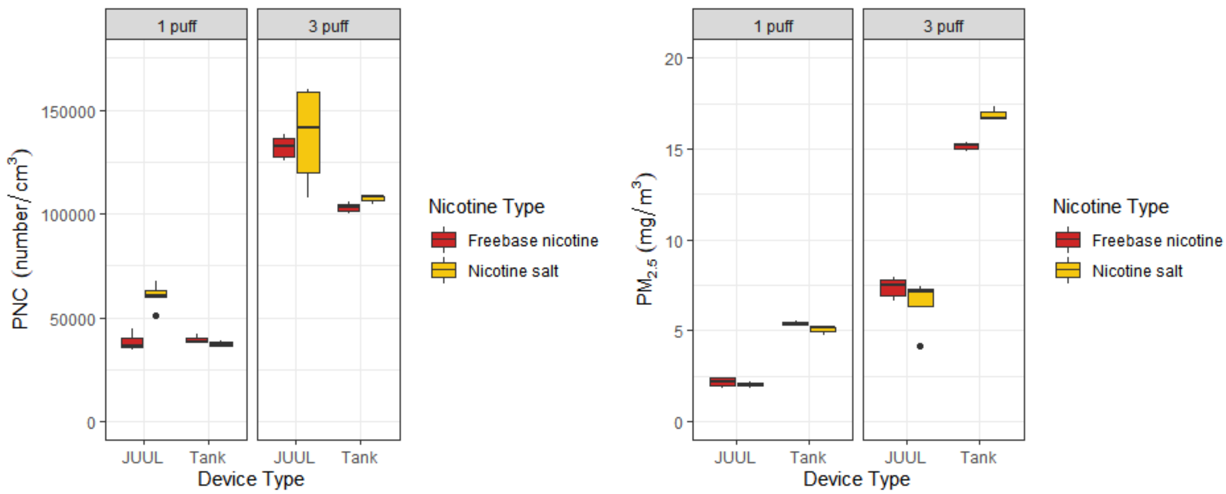
With $\theta_i(t)$ defined as the contact angle of the particle i at a given time t, and θ_{i0} being the contact angle of the particle i at the initial time t_0. In every puffing sample, the frequency distribution of K_i was fitted using a Gaussian distribution. The mean of the fitted distribution was then defined as the volatility constant of the aerosols in an aerosol sample. The closer $|\overline{K_i}|$ (absolute value of the fitted mean of K_i) value is to 0, the less volatile the aerosols are.

3. Results and discussions:

3.1. Summary of PNC and $PM_{2.5}$

The box plot of PNC and $PM_{2.5}$ concentrations were shown in Figure 3. The PNC and $PM_{2.5}$ levels for both JUUL and tank devices were comparable with the values reported in previous studies (Li et al., 2020; Luo et al., 2021; Protano et al., 2020). These concentrations roughly tripled from one puff to three puffs, indicating that the puffing system was consistent between different replications of experiments.

In the 1-puff groups shown in Figure 3 (a), PNC generated from JUUL with nicotine salt in e-liquids were significantly higher than the other three groups ($p<0.0001$), while the other three groups had no significant differences. In 3-puff groups, using the same device, no significant differences for PNC were observed between freebase nicotine and nicotine salt groups. On the contrary, PNC between JUUL and tank devices were statistically significant ($p<0.01$). The variation of $PM_{2.5}$ level between devices was more remarkable than PNC. $PM_{2.5}$ mass generated from tank devices was more than twice as much as JUUL devices using the same kind of liquid ($p<0.001$). At the same time, the difference in $PM_{2.5}$ mass between the two nicotine types was not statistically significant. Overall, despite that PNC produced by JUUL and tanks were at a comparable level, JUUL aerosols may contain more nanoparticles (particle diameter < 0.1 μm) than its tank counterparts that contribute to less aerosol mass.

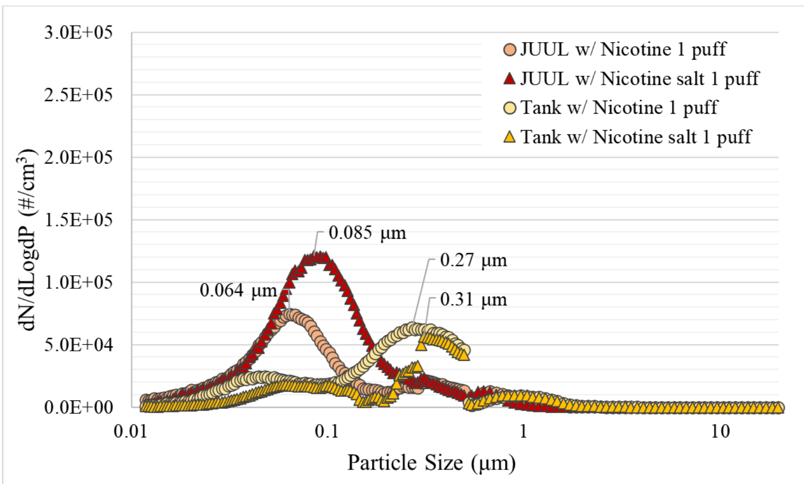


(a) PNC (b) $PM_{2.5}$

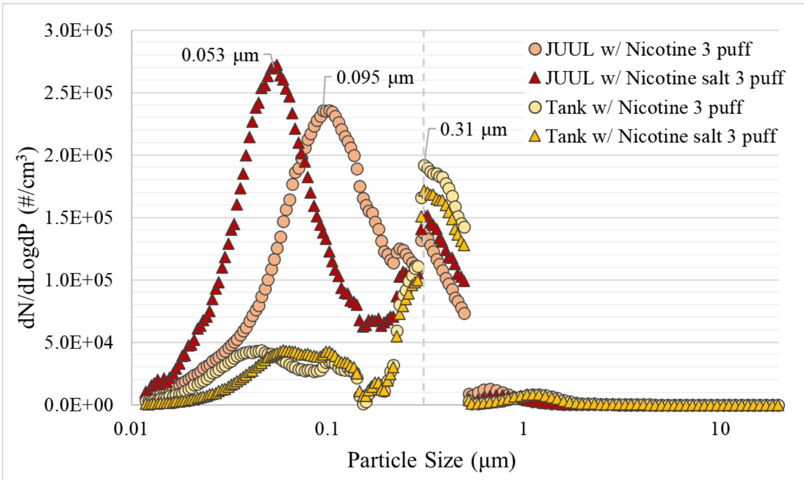
<u>Figure 3.</u> Box plot of (a) PNC and (b) $PM_{2.5}$ of the e-cig aerosol.

3.2 Particle size distributions

Figures 5 plotted the particle size distributions ($\frac{dN}{dlogd_p}$) in a total of 157 size bins measured by APS and SMPS. In Figure 5 (a), 1-puff samples from both JUUL and tank devices were unimodal, with their modes at 0.06-0.09 μm and 0.27-0.31 μm, respectively. For 3-puff tank device samples, a notable single mode was observed at 0.31 μm. Nevertheless, size distributions from 3-puff JUUL samples were more likely to be bimodal, with the first mode at 0.06-0.1 μm, and the second mode at 0.31 μm. With the same kind of device, the shape of distribution was similar for nicotine and nicotine salt except for the shift of the first particle mode. In all but JUUL 3-puff samples, the first particle mode for nicotine salt samples was greater than pure nicotine samples. E-cig device also brings more changes to the shape of particle size distribution curve than nicotine source in e-liquids. Despite that both devices have a common peak at 0.31 µm, tank devices generated almost twice as much $d_p > 0.1$ µm particles than JUUL pods, while JUUL pods have the majority of particles in the ultrafine particle range ($d_p < 0.1$ µm). Additionally, comparing the peaks at 0.31 µm between 1-puff and 3-puff samples, the sharp increase for peak PNC for 3-puff samples (in Figure 5 (b) and (d)) indicated that particle coagulation might have occurred in the 3-puff samples, i.e., smaller particles collided and adhered to each other to form larger particles.



(a)



(b)

<u>Figure 4.</u> Particle size distributions of (a) 1-puff (b) 3-puff samples from JUUL and tank devices, with freebase nicotine and nicotine salt in the e-liquid.

3.3 linear mixed model results

The results of the fitted linear mixed model were shown in Table 3, with 1-puff samples and 3-puff samples analyzed in two separate models. For 1-puff samples in Table 3 (a), nicotine type had a much greater effect on PNC and being statistically significant ($p<0.001$), which may be due to the high PNC in the JUUL-nicotine salt group. For 3-puff samples in Table 3 (b), both device type and nicotine type had no statistically significant impacts on PNC (p-value was 0.093 and 0.534, respectively). However, device type and nicotine type may have a synergistic effect ($p<0.05$) on $PM_{2.5}$ mass concentration, meaning that the effect on $PM_{2.5}$ by changing from pure nicotine to nicotine salt is much greater on tank than on JUUL devices. For both 1-puff and 3-puff samples, device type had a dominant effect on $PM_{2.5}$ mass concentration and was statistically significant ($p<0.001$), which also matched the conclusions in section 3.1 and 3.2. For PNC of 3-puff samples, the conditional R^2 was marked as "NA" as sampling date was not tested significant as a random-effects variable in this case. For $PM_{2.5}$ values, the conditional R^2 values reached 0.964 and 0.99 and marginal R^2 were at 0.964. This indicated that the mixed-effects model could explain 99% and 96.4% of the variation of the $PM_{2.5}$ levels for 1-puff and 3-puff samples, respectively, and the fixed-effects models could explain 96.4% of the variation. The diagnostic graphs, including the residual plot and Q-Q plot, were included in Supplementary figure S3.

Table 1. Linear mixed-effects model results for (a) 1-puff samples and (b) 3-puff samples.

(a) 1-puff samples

Y variable	Fixed Effects X Variable	Description of X Variable	Coefficient	Standard error	p-value[a]	Conditional R^2	Marginal R^2
PNC	DEVICE	Device type	-2950.5	3520.3	0.420	0.922	0.804
	Nic	Nicotine type in the e-liquid	20732.3	2669.3	**<0.001*** **		
	DEVICE:Nic	Interaction term between device type and nicotine type	-19988.0	6687.5	0.096		
$PM_{2.5}$	DEVICE	Device type	3.4	0.2	**<0.001*** **	0.99	0.964
	Nic	Nicotine type in the e-liquid	0.1	0.1	0.557		
	DEVICE:Nic	Interaction term between device type and nicotine type	-0.5	0.4	0.299		

(b) 3-puff samples

Y variable	Fixed Effects X Variable	Description of X Variable	Coefficient	Standard error	p-value[a]	Conditional R^2	Marginal R^2
PNC	DEVICE	Device type	-28870.2	9471.4	0.093	NA	0.549
	Nic	Nicotine type in the e-liquid	5569.2	8646.2	0.534		
	DEVICE:Nic	Interaction term between device type and nicotine type	-1627.5	13941.5	0.909		
$PM_{2.5}$	DEVICE	Device type	7.7	0.4	**0.0064** **	0.964	0.964
	Nic	Nicotine type in the e-liquid	-0.9	0.6	0.143		
	DEVICE:Nic	Interaction term between device type and nicotine type	2.7	0.9	**0.0157***		

[a]Significance codes: * <0.05; ** <0.01; ***<0.001.

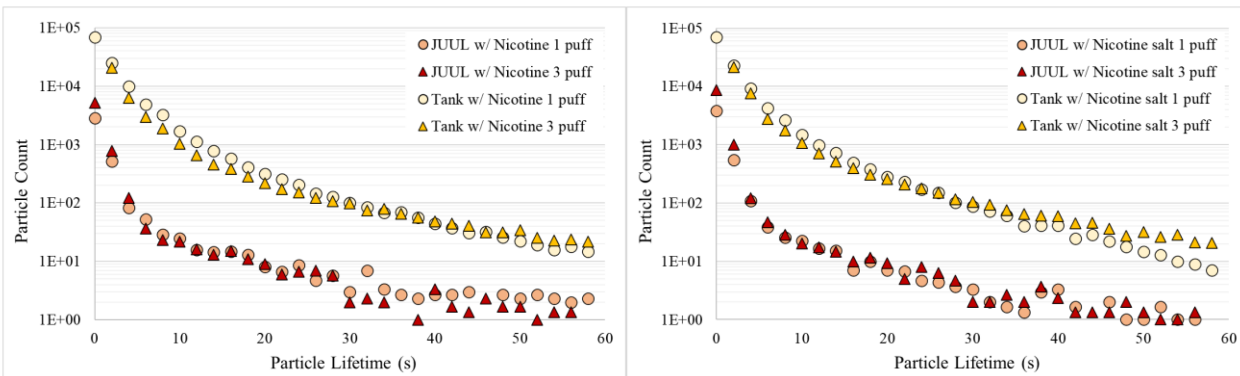
3.4 Distributions of particle lifetime and volatility

The histogram of particle lifetime and volatility were presented in Figures 5 and 6, respectively. In Figure 5, for all eight experimental conditions, >95% of the particles had lifetimes less than 60 seconds, which agreed with previous studies that categorized e-cigarette aerosols as "high volatility" or "semi-volatile" aerosols (Fisenko et al., 2021; Li et al., 2020; Wallace et al., 2021). There were no substantial variations of particle lifetime distribution between nicotine and nicotine salt e-liquids. However, compared to tank device aerosols, JUUL aerosols contained substantially more particles whose lifetimes are less than 10 seconds. Additionally, there was almost no difference for the lifetime of JUUL particles when puff number was increased. However, for tank devices, particles having lifetimes greater than 40 seconds had a notable increase from 1 puff to 3 puffs, especially for tank e-cig with nicotine salt (see Figure 5 (b)).

For particle volatility, device type is also a more substantial factor than the nicotine type in the e-liquids, as shown in Figure 6. Particle volatility distribution between the two types of nicotine only showed slight differences. However, compared to JUUL aerosols, aerosols from tank devices exhibited a distinctly different volatility distribution and were significantly less volatile ($p < 0.05$). Another major difference between tank device and JUUL aerosols is the change of volatility with the increase of emission level. When the number of puffs was increased from 1 to 3, volatility for tank device aerosols had a sharp decrease while this number for JUUL was not significantly changing (Figure 6 (d) and (f)). This volatility shift may result from the mass accumulation of tank device aerosols in the air and collection surface. According to the Kelvin effect, smaller particles may have greater volatility as the curvature of the surface modified the equilibrium partial pressure on the liquid surface (Hinds, 1999). In the results of

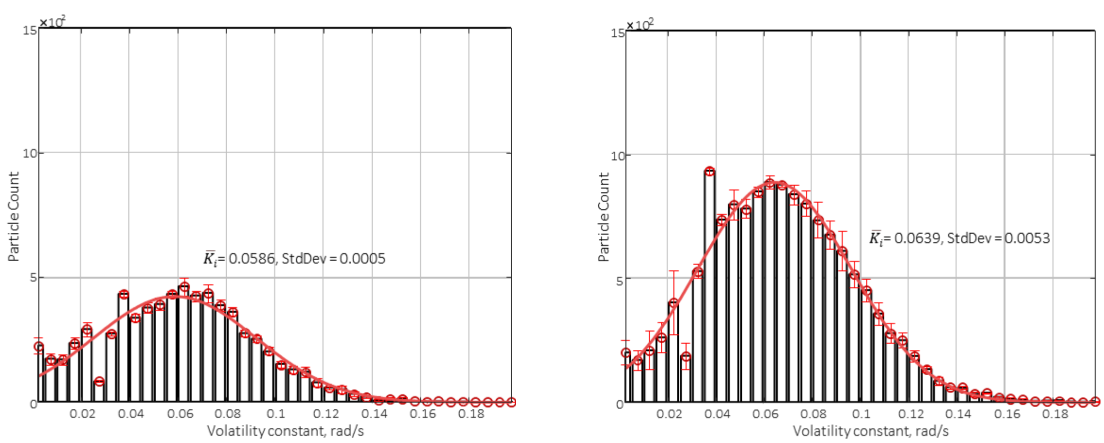
Wallace (2021), puff number was reported as a dominant variable of the decay rate of particle mass and the volatile particle fraction. The authors also discussed "large mass accumulation" scenarios, i.e., particle mass accumulation rate exceed 1000 ng/min (1 μg/min), in which particle mass decay rate and volatile fraction were substantially lowered. For the tank device used in this study, the particle emission factor using a similar e-liquid (30%PG/70%VG/2.4% nicotine) was reported at 172 μg/puff (344 μg/min for the current puffing topography), which is more than 300 times higher than the threshold of the "large mass accumulation" in Wallace et al. study (Li et al., 2020). As puff number increased from 1 to 3 for tank device, the generation of 0.3-μm sized particles and the coagulation of smaller particles shifted the aerosol distribution to contain more larger particles that were inherently less volatile. For JUUL aerosols that contain more ultrafine particles, it is still possible to witness particle volatility decrease due to Kelvin effect, but only at a much higher puff number and particle mass concentration. A more detailed relationship between particle size distribution and particle volatility for the aerosols remains unclear in this study. To further explore this phenomenon, more experiments need to be conducted at a more comprehensive list of emission levels for both kinds of devices and nicotine types.

Apart from the effect of particle size, particle chemical composition may also play a role in determining particle volatility. During the aerosolization process, PG and VG in the e-liquids may undergo thermal degradation upon their contact with the heating element in the device, forming volatile carbonyl compounds, such as formaldehyde, acetaldehyde, acrolein and acetone (Bekki et al., 2014; Geiss et al., 2016; Kosmider et al., 2018; Reilly et al., 2019; Sleiman et al., 2016). These carbonyl compounds and their acidic derivatives may continue to react with nicotine and reduce particle volatility in e-cig aerosol (El-Hellani et al., 2018; Jensen et al., 2017; Schober et al., 2014). Although the same e-liquids were used in JUUL and tank devices, the liquid may be heated to different temperatures with different contact surface areas and different durations in two distinctly different devices (Zhao et al., 2016). Device wattage may also affect the heating temperature in atomizers (Kosmider et al., 2018; Sleiman et al., 2016; Talih et al., 2017). As a result, the level of thermal degradation products in the e-cig aerosols may vary substantially with device type, thus warrants future studies.

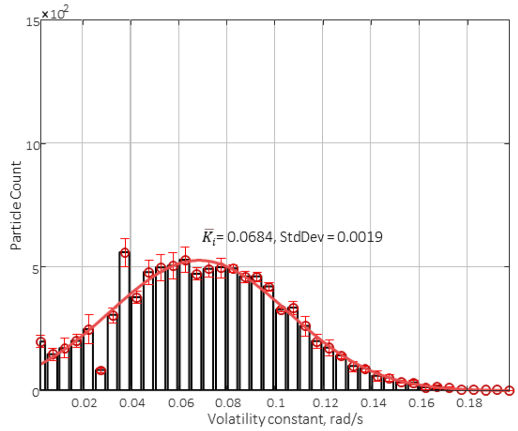


(a) e-liquids with freebase nicotine (b) e-liquids with nicotine salt

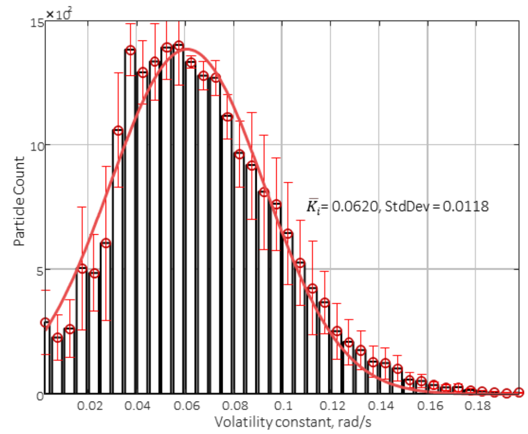
<u>Figure 5.</u> Histogram of average e-cigarette particle lifetime (in seconds) on the c-Air impactor, with (a) e-liquids with freebase nicotine; (b) e-liquids with nicotine salt;



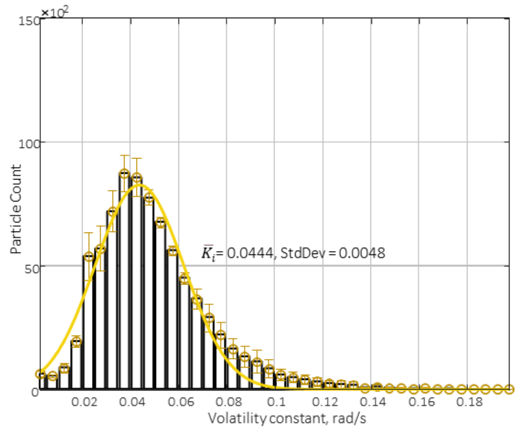
(a) JUUL pods with freebase nicotine, 1 puff (b) JUUL pods with freebase nicotine, 3 puff



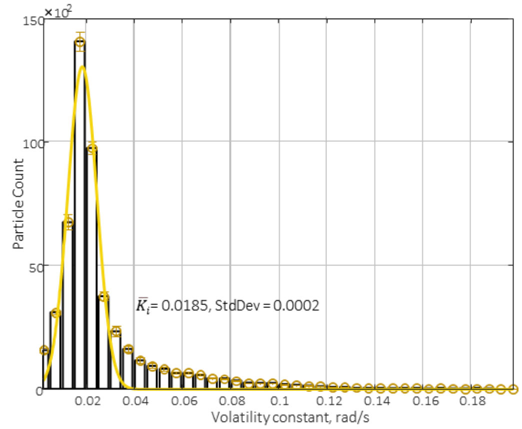
(c) JUUL pods with nicotine salt, 1 puff



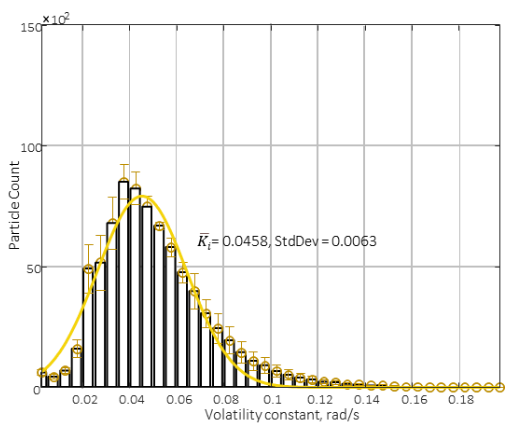
(d) JUUL pods with nicotine salt, 3 puff



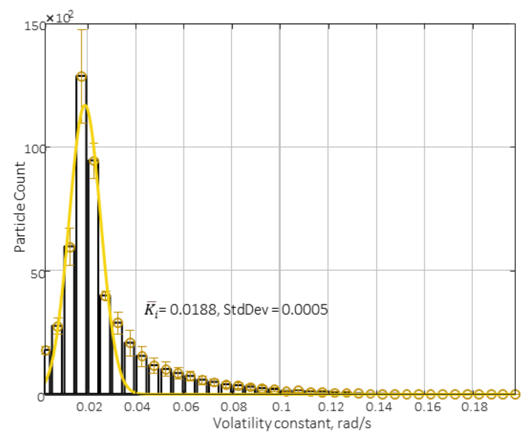
(e) Tank e-cigs with freebase nicotine, 1 puff



(f) Tank e-cigs with freebase nicotine, 3 puff



(g) Tank e-cigs with nicotine salt, 1 puff



(h) Tank e-cigs with nicotine salt, 3 puff

Figure 6. Histogram of e-cigarette particle volatility (in rad/s).

4. Conclusions:

This study provided new data to demonstrate that the environmental vaping exposure could vary substantially between different generations and types of e-cig devices, even when using the same e-liquid. The data suggested that despite that JUUL and tank device produced comparable PNC, tank devices is a more potent source of $PM_{2.5}$. The increase of puffing number shifted particle size distribution to have more 0.3-μm particles for both devices. For tank devices, particles may also coagulate and become significantly less volatile when the puffing number was increased. In indoor environments, repetitive puffing of tank devices may substantially increase the user exposure as particles accumulate in the air and their volatility decreased.

Despite that JUUL is the brand that currently have the largest e-cig market share in the US, more research attention is needed to examine the aerosol characteristics from other popular new-generation e-cig products (such as Puff Bar, Vuse and SMOK) on the market, particularly on how these characteristics change with puff number and environmental conditions (Statista, 2020; Centers for Disease Control and Prevention [CDC], 2016). Additionally, there is a research need to evaluate the difference of particle characteristics between mainstream and exhaled aerosols for JUUL devices to further characterize the human exposure to JUUL aerosols in the environment. Finally, the association between the particle characteristics and potential health effects for JUUL aerosols need to be further validated by toxicological assay studies.

5. Appendices

Table S1. Summary of PNC and $PM_{2.5}$ mass concentration of the e-cig aerosols

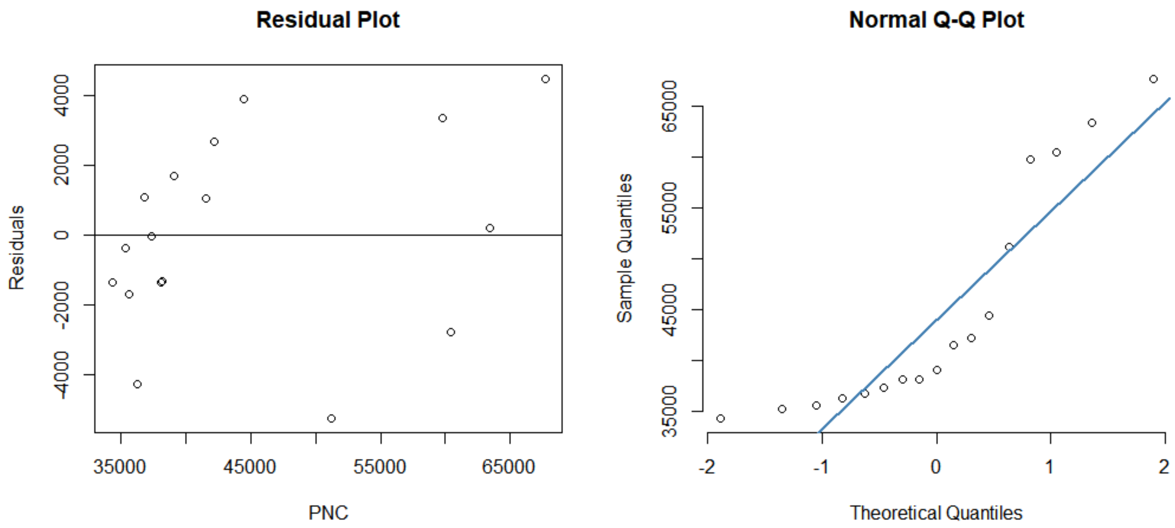
Number of puffs	Device	Nicotine type	PNC (#/cm^3)[a]	$PM_{2.5}$ (μg/m^3)[a]
1 puff	JUUL	Freebase nicotine	$3.81\times10^4 \pm 3.98\times10^3$	2.16 ± 0.27
		Nicotine salt	$6.05 \times10^4 \pm 6.06\times10^3$	2.04 ± 0.14
	Tank	Freebase nicotine	$3.95\times10^4 \pm 2.32\times10^3$	5.37 ± 0.15
		Nicotine salt	$3.32\times10^4 \pm 4.63\times10^3$	4.90 ± 0.24
3 puffs	JUUL	Freebase nicotine	$1.32\times10^5 \pm 5.33\times10^3$	7.39 ± 0.56
		Nicotine salt	$1.37\times10^5 \pm 6.29\times10^4$	6.49 ± 3.14
	Tank	Freebase nicotine	$1.03\times10^5 \pm 2.81\times10^3$	15.13 ± 0.28
		Nicotine salt	$1.07\times10^5 \pm 2.31\times10^3$	16.89 ± 0.42

[a]Values expressed in mean ± standard deviation.

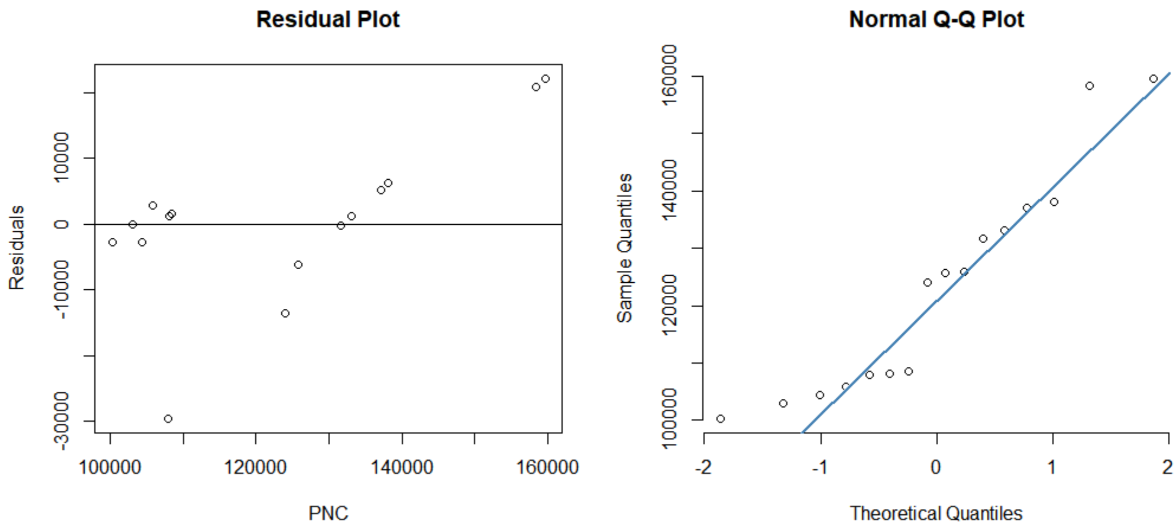
Table S2. Summary of volatility constants of the e-cig aerosols

Number of puffs	Device	Nicotine type	Volatility constant[a]
1 puff	JUUL	Freebase nicotine	0.0586 ± 0.0005
		Nicotine salt	0.0684 ± 0.0019
	Tank	Freebase nicotine	0.0444 ± 0.0048
		Nicotine salt	0.0458 ± 0.0063
3 puffs	JUUL	Freebase nicotine	0.0639 ± 0.0053
		Nicotine salt	0.0620 ± 0.0118
	Tank	Freebase nicotine	0.0185 ± 0.0002
		Nicotine salt	0.0188 ± 0.0005

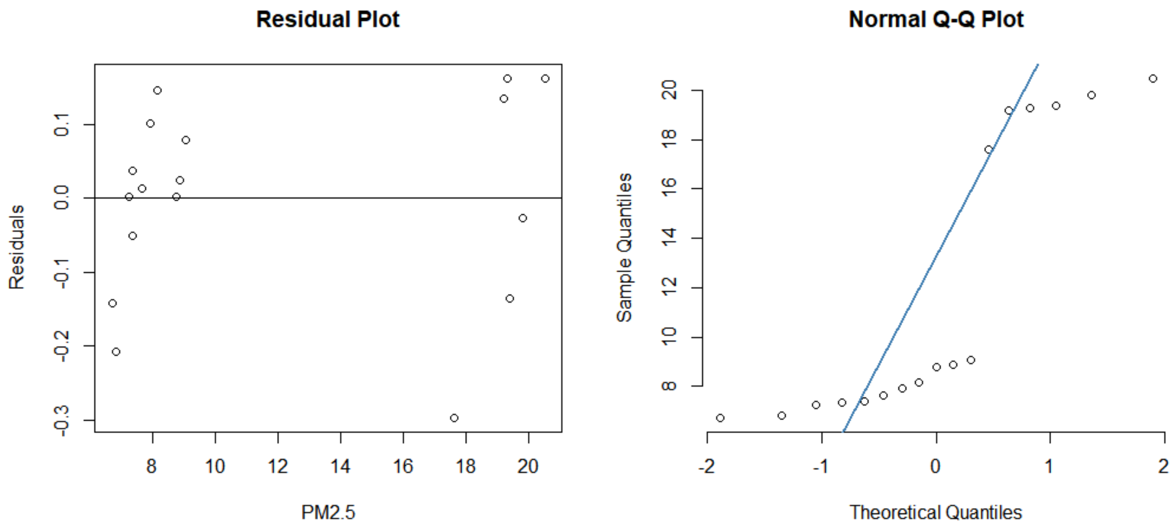
[a]Values expressed in mean ± standard deviation.



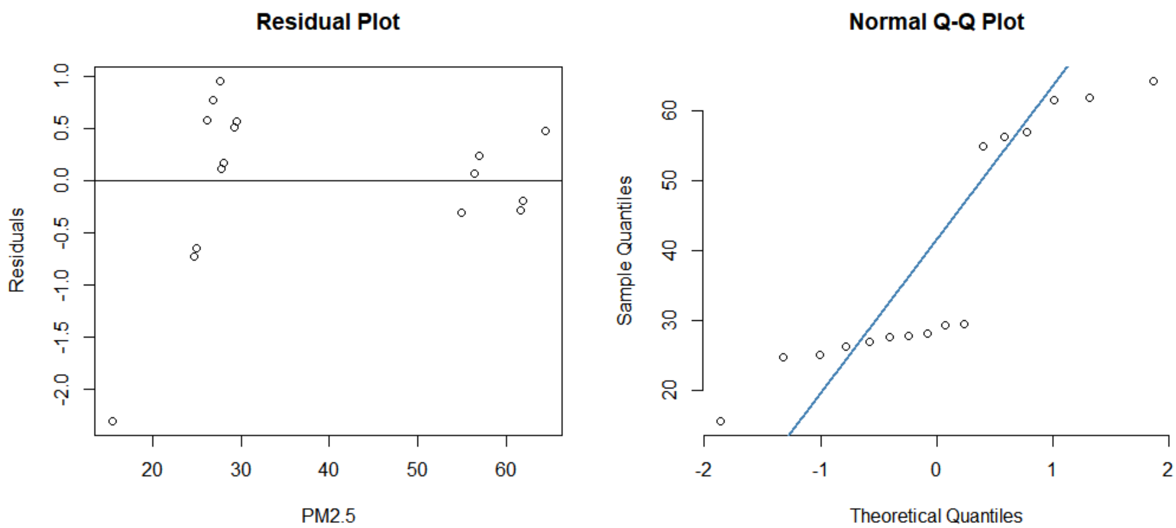
(a) 1-puff samples, PNC



(b) 3-puff samples, PNC



(c) 1-puff samples, $PM_{2.5}$



(d) 3-puff samples, $PM_{2.5}$

<u>Figure S3.</u> Diagnostic graphs of the fitted linear mixed-effects model.

6. References

Baweja, R., Curci, K. M., Yingst, J., Veldheer, S., Hrabovsky, S., Wilson, S. J., Nichols, T. T., Eissenberg, T., & Foulds, J. (2016). Views of experienced electronic cigarette users. In *Addiction Research and Theory* (Vol. 24, Issue 1, pp. 80–88). https://doi.org/10.3109/16066359.2015.1077947

Behar, R. Z., Hua, M., & Talbot, P. (2015). Puffing topography and nicotine intake of electronic cigarette users. *PLoS ONE*, *10*(2). https://doi.org/10.1371/journal.pone.0117222

Bekki, K., Uchiyama, S., Ohta, K., Inaba, Y., Nakagome, H., & Kunugita, N. (2014). Carbonyl compounds generated from electronic cigarettes. In *International Journal of Environmental Research and Public Health* (Vol. 11, Issue 11, pp. 11192–11200). MDPI AG. https://doi.org/10.3390/ijerph111111192

Bowen, A., Xing, C., Juul Labs Inc. (2015). Nicotine salt formulations for aerosol devices and methods thereof, US Patent No. US20150020824A1. Washington, DC: US Patent and Trademark Office.

Centers for Disease Control and Prevention. (2016). *E-Cigarette Use Among Youth and Young Adults. A Report of the Surgeon General*. Department of Health and Human Services, National Center for Chronic Disease Prevention and Health Promotion, Office on Smoking and Health. https://www.cdc.gov/tobacco/data_statistics/sgr/e-cigarettes/index.htm

Dai, H., & Hao, J. (2020). Online popularity of JUUL and Puff Bars in the USA: 2019-2020. *Tobacco Control*. https://doi.org/10.1136/tobaccocontrol-2020-055727

Davies, J. F., Haddrell, A. E., & Reid, J. P. (2012). Time-resolved measurements of the evaporation of volatile components from single aerosol droplets. *Aerosol Science and Technology*, *46*(6), 666–677. https://doi.org/10.1080/02786826.2011.652750

El-Hellani, A., Bs, R. S., El-Hage, R., Talih Phd, S., Malek, N., Baalbaki, R., Karaoghlanian Be, N., Nakkash Phd, R., Scd, A. S., & Saliba, N. A. (2018). Nicotine and Carbonyl Emissions From Popular Electronic Cigarette Products: Correlation to Liquid Composition and Design Characteristics. *Nicotine & Tobacco Research*, 215–223. https://doi.org/10.1093/ntr/ntw280

Fang, X., Li, B., Petersen, E., Ji, Y., Sokolov, J. C., & Rafailovich, M. H. (2005). Factors controlling the drop evaporation constant. *Journal of Physical Chemistry B*, *109*(43), 20554–20557. https://doi.org/10.1021/jp053986d

Farsalinos, K. E., Romagna, G., Tsiapras, D., Kyrzopoulos, S., & Voudris, V. (2013). Evaluation of electronic cigarette use (Vaping) topography and estimation of liquid consumption: Implications for research protocol standards definition and for public health authorities' regulation. *International Journal of Environmental Research and Public Health*, *10*(6), 2500–2514. https://doi.org/10.3390/ijerph10062500

Fisenko, S. P., Rostami, A. A., Kane, D. B., Pithawalla, Y. B., Maximoff, S. N., Li, W., & El-Shall, M. S. (2021). Model of aerosol evolution in high supersaturated glycerol-air vapor mixtures. *Aerosol Science and Technology*, 1–21. https://doi.org/10.1080/02786826.2021.1904130

Geiss, O., Bianchi, I., & Barrero-Moreno, J. (2016). Correlation of volatile carbonyl yields emitted by e-cigarettes with the temperature of the heating coil and the perceived sensorial quality of the generated vapours. *International Journal of Hygiene and Environmental Health*, *219*(3), 268–277. https://doi.org/10.1016/j.ijheh.2016.01.004

Glantz, S. A., & Bareham, D. W. (2018). E-Cigarettes: Use, Effects on Smoking, Risks, and Policy Implications. In *Annual Review of Public Health* (Vol. 39, pp. 215–235). https://doi.org/10.1146/annurev-publhealth-040617-013757

Goniewicz, M. L., Boykan, R., Messina, C. R., Eliscu, A., & Tolentino, J. (2019). High exposure to nicotine among adolescents who use Juul and other vape pod systems (pods'). In *Tobacco Control* (Vol. 28, Issue 6, pp. 676–677). https://doi.org/10.1136/tobaccocontrol-2018-054565

Hinds, W.C., (1999). Aerosol Technology: Properties, Behavior, and Measurement of Airborne Particles. John Wiley & Sons.

Huang, J., Duan, Z., Kwok, J., Binns, S., Vera, L. E., Kim, Y., Szczypka, G., & Emery, S. L. (2019). Vaping versus JUULing: How the extraordinary growth and marketing of JUUL transformed the US retail e-cigarette market. *Tobacco Control*, *28*(2), 146–151. https://doi.org/10.1136/tobaccocontrol-2018-054382

Ingebrethsen, B. J., Cole, S. K., & Alderman, S. L. (2012). Electronic cigarette aerosol particle size distribution measurements. *Inhalation Toxicology*, *24*(14), 976–984. https://doi.org/10.3109/08958378.2012.744781

Jensen, R. P., Strongin, R. M., & Peyton, D. H. (2017). Solvent Chemistry in the Electronic Cigarette Reaction Vessel. *Scientific Reports*, *7*. https://doi.org/10.1038/srep42549

Kosmider, L., Spindle, T. R., Gawron, M., Sobczak, A., & Goniewicz, M. L. (2018). Nicotine emissions from electronic cigarettes: Individual and interactive effects of propylene glycol to vegetable glycerin composition and device power output. *Food and Chemical Toxicology*, *115*, 302–305. https://doi.org/10.1016/j.fct.2018.03.025

Li, L., Lee, E. S., Nguyen, C., & Zhu, Y. (2020). Effects of propylene glycol, vegetable glycerin, and nicotine on emissions and dynamics of electronic cigarette aerosols. *Aerosol Science and Technology*, *54*(11), 1270–1281. https://doi.org/10.1080/02786826.2020.1771270

Li, L., Lin, Y., Xia, T., & Zhu, Y. (2019). Effects of electronic cigarettes on indoor air quality and health. In *Annual Review of Public Health* (Vol. 41, pp. 363–380). https://doi.org/10.1146/annurev-publhealth-040119-094043

Luo, Y., Wu, Y., Li, L., Guo, Y., Çetintaş, E., Zhu, Y., & Ozcan, A. (2021). Dynamic Imaging and Characterization of Volatile Aerosols in E-Cigarette Emissions Using Deep Learning-

Based Holographic Microscopy. *ACS Sensors*, *6*(6), 2403–2410. https://doi.org/10.1021/acssensors.1c00628

Mathur, A., & Dempsey, O. J. (2018). Electronic cigarettes: A brief update. In *Journal of the Royal College of Physicians of Edinburgh* (Vol. 48, Issue 4, pp. 346–351). https://doi.org/10.4997/JRCPE.2018.415

McKelvey, K., Baiocchi, M., & Halpern-Felsher, B. (2018). Adolescents' and Young Adults' Use and Perceptions of Pod-Based Electronic Cigarettes. *JAMA Network Open*, *1*(6), e183535. https://doi.org/10.1001/jamanetworkopen.2018.3535

Melstrom, P., Koszowski, B., Thanner, M. H., Hoh, E., King, B., Bunnell, R., & McAfee, T. (2017). Measuring PM2.5, ultrafine particles, nicotine air and wipe samples following the use of electronic cigarettes. *Nicotine and Tobacco Research*, *19*(9), 1055–1061. https://doi.org/10.1093/ntr/ntx058

Nguyen, C., Li, L., Sen, C. A., Ronquillo, E., & Zhu, Y. (2019). Fine and ultrafine particles concentrations in vape shops. *Atmospheric Environment*, *211*, 159–169. https://doi.org/10.1016/j.atmosenv.2019.05.015

Oldham, M. J., Sehgal, A., Cohen, G., Chen, J., Evans, B., & Heraldez, D. (2021). Room air constituent concentrations from use of electronic nicotine delivery systems and cigarettes using different ventilation conditions. *Scientific Reports*, *11*(1), 1736. https://doi.org/10.1038/s41598-021-80963-9

Oldham, M. J., Zhang, J., Rusyniak, M. J., Kane, D. B., & Gardner, W. P. (2018). Particle size distribution of selected electronic nicotine delivery system products. *Food and Chemical Toxicology*, *113*, 236–240. https://doi.org/10.1016/j.fct.2018.01.045

Pinheiro, J., Bates, D., DebRoy, S., Sarkar, D., R Core Team (2021). nlme: Linear and Nonlinear Mixed Effects Models. R package version 3.1-152. https://CRAN.R-project.org/package=nlme

Protano, C., Avino, P., Manigrasso, M., Vivaldi, V., Perna, F., Valeriani, F., & Vitali, M. (2018). Environmental electronic vape exposure from four different generations of electronic cigarettes: Airborne particulate matter levels. *International Journal of Environmental Research and Public Health*, *15*(10). https://doi.org/10.3390/ijerph15102172

Protano, C., Manigrasso, M., Cammalleri, V., Zoccai, G. B., Frati, G., Avino, P., & Vitali, M. (2020). Impact of electronic alternatives to tobacco cigarettes on indoor air particular matter levels. *International Journal of Environmental Research and Public Health*, *17*(8). https://doi.org/10.3390/ijerph17082947

Reilly, S. M., Bitzer, Z. T., Goel, R., Trushin, N., & Richie, J. P. (2019). Free Radical, Carbonyl, and Nicotine Levels Produced by Juul Electronic Cigarettes. *Nicotine and Tobacco Research*, *21*(9), 1274–1278. https://doi.org/10.1093/ntr/nty221

Robinson, R. J., Hensel, E. C., Morabito, P. N., & Roundtree, K. A. (2015). Electronic cigarette topography in the natural environment. *PLoS ONE*, *10*(6), 1–14. https://doi.org/10.1371/journal.pone.0129296

Schober, W., Szendrei, K., Matzen, W., Osiander-Fuchs, H., Heitmann, D., Schettgen, T., Jörres, R. A., & Fromme, H. (2014). Use of electronic cigarettes (e-cigarettes) impairs indoor air quality and increases FeNO levels of e-cigarette consumers. *International Journal of Hygiene and Environmental Health*, *217*(6), 628–637. https://doi.org/10.1016/j.ijheh.2013.11.003

Schripp, T., Markewitz, D., Uhde, E., & Salthammer, T. (2013). Does e-cigarette consumption cause passive vaping? *Indoor Air*, *23*(1), 25–31. https://doi.org/10.1111/j.1600-0668.2012.00792.x

Shanahan, M. E. R., & Bourgès, C. (1994). Effects of evaporation on contact angles on polymer surfaces. *International Journal of Adhesion and Adhesives*, *14*(3), 201–205. https://doi.org/10.1016/0143-7496(94)90031-0

Sleiman, M., Logue, J. M., Montesinos, V. N., Russell, M. L., Litter, M. I., Gundel, L. A., & Destaillats, H. (2016). Emissions from electronic cigarettes: Key parameters affecting the release of harmful chemicals. *Environmental Science and Technology*, *50*(17), 9644–9651. https://doi.org/10.1021/acs.est.6b01741

Soule, E. K., Maloney, S. F., & Spindle, T. R. (2017). Electronic cigarette use and indoor air quality in a natural setting. *Tob Control*, *26*, 109–112. https://doi.org/10.1136/tobaccocontrol-2015-052772

Statista. (2020). Dollar share of e-cigarette sales in the United States in 2020, by brand.

Retrieved from https://www.statista.com/statistics/1097004/e-cigarette-market-share-us-by-brand/

Talih, S., Balhas, Z., Eissenberg, T., Salman, R., Karaoghlanian, N., Hellani, A. el, Baalbaki, R., Saliba, N., & Shihadeh, A. (2015). Effects of user puff topography, device voltage, and liquid nicotine concentration on electronic cigarette nicotine yield: Measurements and model predictions. *Nicotine and Tobacco Research*, *17*(2), 150–157. https://doi.org/10.1093/ntr/ntu174

Talih, S., Salman, R., El-Hage, R., Karam, E., Karaoghlanian, N., El-Hellani, A., Saliba, N., & Shihadeh, A. (2019). Characteristics and toxicant emissions of JUUL electronic cigarettes. *Tobacco Control*, *28*(6), 678–680. https://doi.org/10.1136/tobaccocontrol-2018-054616

Talih, S., Salman, R., Karaoghlanian, N., El-Hellani, A., Saliba, N., Eissenberg, T., & Shihadeh, A. (2017). Juice Monsters: Sub-Ohm Vaping and Toxic Volatile Aldehyde Emissions. *Chemical Research in Toxicology*, *30*(10), 1791–1793. https://doi.org/10.1021/acs.chemrestox.7b00212 van der Heijden, T. W. G., Darhuber, A. A., & van der Schoot, P. (2018). Macroscopic Model for Sessile Droplet Evaporation on a Flat Surface [Research-article]. *Langmuir*, *34*(41), 12471–12481. https://doi.org/10.1021/acs.langmuir.8b02374

Volesky, K. D., Maki, A., Scherf, C., Watson, L., van Ryswyk, K., Fraser, B., Weichenthal, S. A., Cassol, E., & Villeneuve, P. J. (2018). The influence of three e-cigarette models on indoor fine and ultrafine particulate matter concentrations under real-world conditions. *Environmental Pollution*, *243*, 882–889. https://doi.org/10.1016/j.envpol.2018.08.069

Wallace, L. A., Ott, W. R., Cheng, K. C., Zhao, T., & Hildemann, L. (2021). Method for estimating the volatility of aerosols using the piezobalance: Examples from vaping e-cigarette and marijuana liquids. *Atmospheric Environment*, *253*, 118379. https://doi.org/10.1016/j.atmosenv.2021.118379

Zhao, T., Shu, S., Guo, Q., & Zhu, Y. (2016). Effects of design parameters and puff topography on heating coil temperature and mainstream aerosols in electronic cigarettes. *Atmospheric Environment*, *134*, 61–69. https://doi.org/10.1016/j.atmosenv.2016.03.027

Zhao, T., Nguyen, C., Lin, C. H., Middlekauff, H. R., Peters, K., Moheimani, R., Guo, Q., & Zhu, Y. (2017). Characteristics of secondhand electronic cigarette aerosols from active human use. *Aerosol Science and Technology*, *51*(12), 1368–1376. https://doi.org/10.1080/02786826.2017.1355548