SOA Formation from Naphthalene, 1-Methylnaphthalene, and 2-Methylnaphthalene Photooxidation

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Abstract

The SOA yield and chemical characteristics of SOA formation from naphthalene and two methyl substituted naphthalenes, 1-methylnaphthalene and 2-methylnaphthalene, were studied for high NO_x, low NO_x, and ultra-low NO_x conditions. The SOA yields are high compared to previous studies for all three PAHs precursors: 1-methylnaphthalene > 2-methylnaphthalene ~ naphthalene for all atmospheric conditions studied. The SOA yields range from 0.03~0.60 for naphthalene, 0.21~1.52 for 1-methylnaphthalene, and 0.34~0.55 for 2-methylnaphthalene under high NO_x with HONO (initial PAH:NO ratio= 0.03~0.17) conditions. The SOA yield ranges from 0.04~0.31 for naphthalene, 0.14~0.72 for 1-methylnaphthalene, and 0.06~0.49 for 2-methylnaphthalene under low NO_x (initial PAH:NO ratio = 0.54~2.20) conditions. SOA yields were substantially greater than 1.0 under H₂O₂ (ultra low NO_x) and low NO_x +H₂O₂ conditions for all three PAH precursors. The system reactivity influenced by OH radicals, NO_x levels, initial PAH/NO ratios, NO₂/NO ratios, and all impacted the SOA formation from the PAH precursors. Fractal-

25 like SOA is observed for the methylnaphthalene isomers during high NO_x photooxidation
26 experiments, implying that researchers studying SOA formation from this precursor must
27 carefully account for particle shape or effective density. A m/z 104 (C₇H₄O⁺, 104.026)
28 peak, consistent with SOA products phthalic acid from earlier studies, was observed as a
29 potential marker of PAH oxidation during HR-ToF-AMS analysis.

30 Key words: SOA yield, m/z 104, naphthalene, methylnaphthalene, PAH, fractal
31 agglomerate

32

33 **1. Introduction**

34 The formation of secondary organic aerosol (SOA) originates from a variety of
35 chemical processes including gas-phase oxidation reactions of organic species, reactions
36 in the particle (condensed) phase and continuing chemistry over multiple generations of
37 oxidation products (Kroll and Seinfeld, 2008). SOA negatively impacts visibility and can
38 affect global radiative forcing through both direct and indirect effects (Kanakidou et al.,
39 2005; Schulz et al., 2006). Additionally, epidemiological evidence shows a significant
40 risk between fine particles and lung cancer, respiratory illness, and cardiovascular disease
41 (Lewtas, 2007).

42 Polycyclic aromatic hydrocarbons (PAHs) are an important source of semivolatile
43 gas-phase anthropogenic emissions. Sources of PAH include incomplete combustion
44 emissions from vehicles (Shah et al., 2005), biomass burning (Conde et al., 2005;
45 Hedberg et al., 2002), cooking (McDonald et al., 2003), evaporation of petroleum
46 products (Jia and Batterman, 2010), gasoline and diesel fuels (Aislabie et al., 1999).

47 Naphthalene and methylnaphthalenes are the most abundant PAH precursor and may be a
48 major unaccounted for source of secondary organic aerosol (SOA) as their contribution to
49 ambient secondary particulate matter is not clearly understood. The California Air
50 Resources Board (CARB) 2010 California Toxic Inventory (CARB, 2013) estimates the
51 total emissions of naphthalene to be ~ 910.7 tons year⁻¹ in California. Average Southern
52 California Air Basin naphthalene concentrations range from 91~445 ng m⁻³ (Eiguren-
53 Fernandez et al., 2004; Lu et al., 2005) with Reisen and Arey reporting much higher
54 naphthalene concentrations in Los Angeles due to heavy traffic emissions than in
55 Riverside (Reisen and Arey, 2005). Pye and Pouliot, 2012 estimated that long-chain
56 alkanes and PAHs accounted for 20~30% of SOA derived from anthropogenic
57 hydrocarbons by Community Multiscale Air Quality (CMAQ) model. Further, Lu et al.
58 simulated the distribution of naphthalene emissions over Southern California using the
59 SMOG airshed model and estimated 10-50 kg day⁻¹grid⁻¹ (5-km by 5-km grid cells) in
60 populated urban areas (Lu et al., 2005). However, current SOA model predictions are
61 based on SOA yields from indoor environmental chamber experiments and emission
62 inventory. It is needed to further examine PAH oxidation under different oxidant
63 condition and integrate SOA yields data into current SOA model.

64   Recent studies have focused on investigating gas-phase chemistry mechanism and
65 particle-phase organic aerosol formation from PAH oxidation. Gas-phase chemistry
66 mechanism and products from OH-initiated reaction of naphthalene and alkylnaphthalene
67 atmospheric oxidation was proposed by Kautzman et al (2010) and Wang et al (2007).
68 Kautzman et al. (2010) proposed naphthalene and alkylnaphthalene oxidation

69 mechanisms for high NO_x with 2-formylcinnaldehyde (30~60% yield) as the major
70 product (Nishino et al., 2012, 2009; Sasaki et al., 1997). Formation of nitronaphthalenes
71 (0.6%), naphthols (10%) and other ring-opening and ring-remaining products were
72 observed from OH radical reaction in the presence of NO_x (Sasaki et al., 1997).
73 Additionally, 4-nitro-1-naphthol, hydroxyl phthalic acid and hydroxyl nitrobenzoic acid
74 have also been observed in both urban organic aerosols and laboratory SOA from PAH-
75 NO_x photooxidation (Kautzman et al., 2010). Further, methylnaphthalenes emitted from
76 primary sources can react with OH radicals and NO_x to produce methylnitronaphthalenes
77 and dicarbonyl derivates, which have been reported as carcinogens and associated with
78 mutagenicity and toxic effects in metabolism reactions (Grosovsky et al., 1999; Lin et al.,
79 2009).

80 SOA yields from PAHs oxidation has been reported by previous studies (Chan et
81 al., 2009; Kautzman et al., 2010; Kleindienst et al., 2012). Chan et al. reported SOA
82 yields for high-NO_x conditions between 0.19 and 0.3 for naphthalene, 0.19 and 0.39 for
83 1-methylnaphthalene, and 0.26 and 0.45 for 2-methylnaphthalene. Under low-NO_x
84 conditions, SOA yields were observed to be 0.73, 0.68, and 0.58 for naphthalene, 1-
85 methylnaphthalene, 2-methylnaphthalene, respectively (Chan et al., 2009). However,
86 lower PAH SOA yields ranging from 0.02 to 0.22 were observed by Shakya and Griffin
87 (2010) for aerosol mass concentrations less than 10 µg m⁻³. Kleindienst et al. (2012)
88 recently reported that naphthalene SOA yields ranging 0.11~0.27 under higher NO_x
89 conditions, which is much lower than reported by Kautzman et al (2010). Further,
90 particle-phase phthalic acid has been reported as a major naphthalene photooxidation

91 product for both NO_x conditions, and has been suggested as a potential tracer of ambient
92 naphthalene SOA (Kautzman et al., 2010) due to large observable quantities (e.g., ~ 14
93 ng m⁻³ in Birmingham, Al).

94 The key question in this study is that what the main factors are driving PAH
95 precursor to form SOA. Previous studies from PAH precursor still lack comprehensive
96 understanding characteristics of PAH SOA formation. Overall, this study aims to (i)
97 investigate the roles of NO_x levels and OH radicals on SOA formation from 2 ring-PAH
98 photooxidation; (ii) characterize chemical and physical properties (e.g., volatility, density
99 of particles and chemical composition characteristics) of SOA formation derived from
100 PAHs.

101 **2. Experimental Methodology**

102 **2.1 Experimental Setup**

103 All experiments were performed in the UCR/CE-CERT environmental chamber
104 described in detail elsewhere (Carter et al., 2005). The facility includes a 6m×6m×12m
105 thermally insulated enclosure continuously flushed with purified air (Aadco 737 series
106 (Cleves, Ohio) air purification system). Inside the enclosure, there are two 90 m³ 2 mil
107 (54 μm) FEP Teflon® film reactors along with four banks of 115 W 4-ft Sylvania 350BL
108 blacklights, NO₂ photolysis rate (also called k_1) is 0.408 min⁻¹. The blacklight emission
109 spectrum of the irradiation system is particularly between 300 nm to 420 nm with peak
110 wavelength of 350 nm, the region where H₂O₂ has an adequate photolysis rate (Carter et
111 al., 1995). The elevation of the top frames of the reactors are controlled by elevators that

slowly move down during the experiments to maintain a positive differential pressure of >0.01 in H_2O thereby reducing likelihood of dilution due to sampling, leaks, and permeation. Prior to inject solid naphthalene ($>99\%$, Sigma Aldrich) and 2-methylnaphthalene ($>97\%$, solid, Sigma-Aldrich) into the oven, naphthalene and 2-methylnaphthalene were prepared by heating up known amount weight and then adhered to glass-wool. Known amount of naphthalene, 1-methylnaphthalene ($>95\%$, liquid, Sigma-Aldrich), 2-methylnaphthalene, and 50% wt hydrogen peroxide (H_2O_2) solution were injected into a glass manifold tube in a $55\text{ }^\circ\text{C} \sim 60\text{ }^\circ\text{C}$ oven, and subsequently flushed into the chamber with purified air for 15 min at 10 L min^{-1} for H_2O_2 and 30 min for PAH, respectively. NO was prepared by filling a calibrated glass bulb with a known pressure of pure NO and then subsequently flushed into the chamber with pure N_2 . Nitrous acid (HONO) was injected as the OH precursor for high NO_x ($\text{NO} >350$ ppb initially) condition experiments. HONO was prepared by adding 10 ml of 1w% NaNO_2 dropwise into 20 ml of 10w% H_2SO_4 aqueous solution (Kautzman et al., 2010). A dry air stream was then passed through the bulb, sending HONO into the chamber. When the NO_2 reached about 100 ppb, the injection of HONO was stopped and then the additional NO was added to reach target concentration. H_2O_2 concentration was calculated based on injection volume, %wt of H_2O_2 , and chamber volume without accounting for injection and chamber losses. Ammonium sulfate seed aerosol was generated as needed by atomization of a $\sim 0.005\text{ M}$ aqueous ammonium sulfate solution.

2.2 Instrumentation

133 Gas phase: Perfluorohexane ($n\text{-C}_6\text{F}_{14}$) was used as an inert chemical tracer. The
134 perfluorohexane and PAH concentrations were monitored using Agilent 6890 (Palo Alto,
135 CA) gas chromatography (GC) equipped with flame ionization detectors (FID) (equipped
136 with: 30 m $\times$ 0.53 mm GS-Alumina column as front detector used for the analysis of light
137 hydrocarbons and perfluorohexane and 30 m $\times$ 0.53 mm DB-5 column as back detector
138 used for the analysis of aromatics). The GC column was temperature programmed from -
139 50° (hold 2.0 min.) to 40°C at a rate of 50°C per minute (hold 1.0 min) then up to 200°C
140 at a rate of 30°C per minute with a 13 minute hold at the upper limit. A second Agilent
141 6890 GC equipped with a thermal desorption system (CDS analytical, ACEM9305,
142 Sorbent Tube MX062171 packed with Tenax-TA/Carbopack/Carbosieve S111) was used
143 for the analysis of low-volatility compounds. The tubes were thermally desorbed at
144 290°C. The column used was a 30 m Restek® Rtx-35 Amine (0.53 mm ID, 1.00 micron).
145 NO and NO_y-NO were measured by a TECO NO_x analyzer while O₃ was measured by a
146 Dasibi Environmental Corp. Model 1003-AH O₃ analyzer. It is noted that NO₂ was
147 indirectly measured by the difference of NO_y and NO. The interferences of HONO, nitric
148 acid (HNO₃), organic nitrates (RONO₂) and peroxyacetyl nitrates (PANs) in NO_y species
149 measurement were not excluded.

150 Particle phase: Particle size distributions between 27 and 686 nm and number
151 concentrations were measured with an Scanning Mobility Particle Sizer (SMPS) built in-
152 house described by Cocker et al., 2001. Aerosol particle density was measured with an
153 Aerosol Particle Mass analyzer (APM, Kanomax model 3600) and a SMPS in series. A
154 detailed description of the APM-SMPS system and data algorithms are described

elsewhere (Malloy et al., 2009; Nakao et al., 2011). Particle volatility was measured with a volatility tandem differential mobility analyzer (VTDMA) (Nakao et al., 2012, 2011; L. Qi et al., 2010; Rader and McMurry, 1986), in which monodisperse particles of mobility diameter D_{mi} are selected by the first differential mobility analyzer (DMA) followed by transport through a Dekati thermodenuder (TD, residence time: ~16 s, at 100 °C or at 150 °C). Then, the particle size after the thermodenuder (D_{mf}) is measured by fitting a log-normal size distribution curve acquired by the second DMA. Volume remaining fraction (VRF) is calculated by $VRF = (D_{mf}/D_{mi})^3$ where D_{mf} is the particle mobility diameter after the TD and D_{mi} is the initial particle size selected. The electrostatic FHNW (Fachhochschule Nordwestschweiz) Transmission Electron Microscopy (TEM) sampler was used to collect particles during select experiments. The particulates were subsequently analyzed by TEM (FEI-PHILIPS CM300) at the UCR Central Facility for Advanced Microscopy and Microanalysis (CFAMM).

Particle chemical composition was analyzed with a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) operating in “W-mode” (Aiken et al., 2008, 2007; DeCarlo et al., 2006). Details of the HR-ToF-AMS and software analysis are described in DeCarlo et al., 2006. The HR-ToF-AMS data was analyzed by HR-ToF-AMS analysis toolkit 1.51H and PIKA module for SQUIRREL version 1.10 H.

2. Results and Discussion

3.1 SOA yields from naphthalene, 1-methylnaphthalene and 2-methylnaphthalene

SOA formation from naphthalene, 1-methylnaphthalene and 2-methylnaphthalene was measured for different gas-phase reactivity conditions in the UCR CE-CERT

177 environmental chamber. SOA yields (Y) for individual ROGs were determined as the
 178 total aerosol formed divided by mass of PAH consumed. Yield was then plotted versus
 179 final organic aerosol mass and fit to the following equation (Odum et al., 1996, 1997):

$$180 \quad Y = M_0 \sum_i \left(\frac{\alpha_i K_{om,i}}{1 + K_{om,i} M_0} \right) \quad \text{eq (1)}$$

181 To obtain the best fit two product ($i=2$) model where α_i and $K_{om,i}$ are the mass-based
 182 stoichiometric coefficient and absorption equilibrium partitioning coefficient of product i ,
 183 respectively.

184 A instantaneous aerosol yield (IAY) (Jiang, 2003) was used to compare with
 185 reported SOA yield. The IAY can be defined as the aerosol yield at a specific M_0 , which
 186 is the slope of a tangent line at the point (ΔROG , M_0) on an experimental M_0 versus
 187 ΔROG curve (Jiang, 2003). In this study, the IAY for each point is at the irradiation time
 188 corresponding to the measured ROG data point.

$$189 \quad \text{IAY} = \frac{d M_0}{d \Delta\text{ROG}} \quad \text{eq (2)}$$

190 All experiments were irradiated (NO_2 photolysis rate (k_1) = 0.408 min^{-1}) under
 191 dry conditions ($\text{RH} < 0.1\%$). Table 1 lists the experimental conditions and SOA yields for
 192 photooxidation experiments conducted for each of the three PAH precursors. The initial
 193 PAH concentration in these experiments ranged from 15 ppb to 68 ppb while initial NO_x
 194 was > 350 ppb for high NO_x experiments and < 100 ppb for low NO_x conditions, and $<<$
 195 1 ppb for H_2O_2 experiments.

196 **3.1.1 High NO_x condition**

197 SOA yield ranged from 0.03~0.60 (naphthalene), 0.21~1.52 (1-
198 methylnaphthalene), and 0.34~0.55 (2-methylnaphthalene) under high NO_x (initial
199 PAHs/NO = 0.03~0.17) conditions (Table 1). HONO was injected into high NO_x
200 experiments to serve as an OH radical source to help increase the reactivity of the
201 experiment. However, the HONO production method also produced additional NO and
202 NO₂ which were injected into the chamber. Since NO₂ concentration was not directly
203 measured by a chemiluminescence NO_x analyzer, possible interference from HONO
204 would lead to higher NO₂. The OH radical produced from HONO and NO₂/NO ratio
205 affects aerosol formation from a given PAH precursor (Figure S1). The lowest SOA yield
206 was observed in the 1732A naphthalene-high NO_x experiment (little HONO injection), an
207 indication of lower OH radicals and NO, and higher NO of 624 ppb, leading to less
208 aerosol formation.

209 To further investigate the effect of NO₂/NO ratios on PAH SOA formation under
210 high NO_x conditions, the relationship between IAYs and NO₂/NO ratios are shown in
211 Figure S2. If the initial NO₂/NO ratios ≤ 0.54 , the IAYs increase as NO₂/NO ratios
212 increase. If the initial NO₂/NO ratios ≥ 0.60 , the NO₂/NO ratios vary as the IAYs increase.
213 As the NO₂/NO ratios increase to a threshold, subsequently they decrease as
214 instantaneous yields increase (e.g., 1623A, 1628A, 1590A), indicating the reaction of
215 NO+RO₂ completely forms RO+NO₂ during the course of experiments. In the presence
216 of NO_x, the effect arises from the chain termination in the RO₂ and NO_x cycles via
217 organic nitrates (RONO₂) production: $\text{RO}_2 + \text{NO} \rightarrow \text{RONO}_2$. RO₂ radicals may also react
218 with NO₂ to form peroxy nitrates (ROONO₂): $\text{RO}_2 + \text{NO}_2 \rightarrow \text{ROONO}_2$. The other possible

219 chain primary termination reaction in PAH oxidation reaction could occur at nitric acid
220 (HNO_3) production in high NO_x region: $\text{OH} + \text{NO}_2 \rightarrow \text{HNO}_3$.

221 The OH radical initiates reactions of alkylnaphthalene/naphthalene mainly by
222 addition to the ring to form an OH-alkylnaphthalene or OH-naphthalene adduct which
223 subsequently reacts with NO_2 or O_2 (Atkinson and Arey, 2007). 1-Methylnaphthalene and
224 2-methylnaphthalene can also undergo additional reactions with OH, namely H-atom
225 abstraction from the methyl group. In this study, SOA yield under high- NO_x conditions is
226 non-linearly related to the HONO, NO, and NO_2 concentrations (Figure S1 and Figure S2),
227 implying that aerosol formation is expected through NO_2 reaction with OH-naphthalene
228 or OH-alkylnaphthalene adducts leading to nitro-containing and other low volatility
229 products. Previous studies have identified ring-opened products from OH-initiated
230 naphthalene or alkylnaphthalene reactions including 2-formylcinnamaldehyde (30-60%),
231 phthalaldialdehyde and phthalic anhydride (Atkinson and Arey, 2007; Nishino et al., 2012,
232 2009). These products can continue to oxidize and form secondary-generation products
233 that could further to partition into the condensed phase.

234 **3.1.2 Low NO_x condition**

235 In the low NO_x (initial PAH/NO = 0.54~2.20) experiments, SOA yield is
236 0.04~0.31, 0.14~0.72, and 0.06~0.49 for naphthalene, 1-methylnaphthalene, and 2-
237 methylnaphthalene, respectively. The photooxidation routes to form SOA are expected to
238 be dominated by $\text{RO}_2 + \text{HO}_2$ and $\text{RO}_2 + \text{NO}$ reaction pathways (Kroll and Seinfeld, 2008).
239 The SOA yield from the PAH precursors under low- NO_x conditions ($\text{NO} < 100\text{ppb}$ and
240 initial PAH/NO ratio = 0.54~ 2.20) is mostly lower than that observed for high NO_x (NO

241 > 400 ppb and initial PAH/NO ratio =0.03~0.17) (3.1.1; see also Figure S1 and Figure S3)
 242 in this study. Figure S3 shows that the initial PAH/NO ratio significantly influences the
 243 SOA growth, which was observed as the initial PAH/NO ratio increases the aerosol
 244 formation increases. For instance, the initial naphthalene/NO ratio is 3.41 for 1828A and
 245 1.26 for 1592A, the aerosol mass produced for 1828A is much higher than 1592A as
 246 shown in Figure S3 (a). The SOA yield increased as initial NO level (< 100 ppb)
 247 decreased which can be attributable to increasing RO₂ and HO₂ radical concentrations
 248 leading to reactions forming products with lower volatilities, similar to observed NO_x
 249 effects on SOA formation from aromatic hydrocarbon (Li et al., 2015). Organic aerosol
 250 does not grow in the early hours of the experiment (e.g., run 1661A) with only slight
 251 aerosol formation observed after 3-5 hours, suggesting NO_x might slowly react with
 252 intermediate radicals forming organic nitrate products.

253 3.1.3 Effect of seed aerosol

254 Ammonium sulfate seed aerosol was introduced to four naphthalene low NO_x
 255 condition photooxidation experiments with particulate mass of organic aerosol
 256 determined by:

$$257 \quad \text{PM mass} = \text{PM}_{(\text{NH}_4)_2\text{SO}_4} \text{ mass} + \text{PM}_{\text{Org}} \text{ mass} + \text{PM}_{\text{NO}_3} \text{ mass} \quad (2)$$

$$258 \quad \text{PM}_{\text{Org}+\text{NO}_3} \text{ mass (t)} = (\text{PM volume corrected} \times \rho(t)) \times (1 - f_{(\text{NH}_4)_2\text{SO}_4}(t)) \quad (3)$$

259 where $f_{(\text{NH}_4)_2\text{SO}_4}$ is the fraction of particulate matter that is ammonium sulfate acquired
 260 by HR-ToF-AMS and obtained from eq(2). Aerosol density as a function of time ($\rho(t)$)
 261 was directly obtained by the APM-SMPS. Thus, total organic and nitrate aerosol mass

262 formed ($\text{PM}_{\text{Org}+\text{NO}_3}$ mass (t)) can be calculated by equation (3). Nitrates also describe the
263 functional group organic nitrates (RONO_2). The aerosol formation in the four seeded
264 experiments agrees well with the non-seeded experiments indicating little loss of semi-
265 volatiles to the chamber walls in contrast to Kautzman et al 2010. This may be due to the
266 large volume of the environmental chamber and the absorption of semi-volatiles to
267 organic matters adsorbed on the inner surface of chamber (Loza et al., 2010). The inner
268 surface of this chamber would be cleaner than that of the chamber used by Kautzman et
269 al 2010.

270 **3.1.4 $\text{H}_2\text{O}_2/\text{H}_2\text{O}_2$ +low NO_x condition**

271 SOA yields in the presence of H_2O_2 increase greatly for naphthalene, 1-
272 methylnaphthalene and 2-methylnaphthalene, with some mass-yields exceeding 1.0. High
273 SOA yields occurred in H_2O_2 (only) irradiation condition (1~2 ppm) due to high OH
274 radical concentrations produced by the blacklights (NO_2 photolysis rate is 0.408 min^{-1}).
275 SOA yield from 1-methylnaphthalene photooxidation is the highest followed by
276 naphthalene and 2-methylnaphthalene. Even higher yields are observed for the low NO_x
277 + H_2O_2 conditions due to even higher OH radical concentrations with SOA which are
278 highest for 1-methylnaphthalene (1.93), followed by 2-methylnaphthalene (1.26), and
279 naphthalene (1.15). The yields obtained from the H_2O_2 experiments suggest the
280 RO_2+HO_2 chemistry produces a substantial amount of low-volatility hydroperoxides and
281 acids. NO quickly drops to sub-ppb levels during the first hour of irradiation (e.g., run:
282 1613A), allowing RO_2 and HO_2 to rapidly build and SOA formation to commence (this is
283 compared with ~ 5 hours for low NO_x experiments when NO depletes and SOA

formation accelerates). Additionally, Figure S1(d) shows a linear relationship between instantaneous aerosol yield (IAY) and M_0 concentration. The PAHs were consumed (>99%) after 3 hours irradiation under low $\text{NO}_x + \text{H}_2\text{O}_2$ conditions (Figure S3 (d)) due to the high OH radical level concentrations. The SOA growth curve (ΔM_0 vs. hydrocarbon reacted ΔHC) indicates that SOA continued to grow after hydrocarbon reacted completely (Figure S3 (d) 1613A) suggesting partitioning of some multigenerational oxidation products.

3.1.5 Overall comparison

SOA yields are much higher in this work than the studies of Chan et al. (2009), Kleindienst et al.(2012), and Shakya et al. (2010) as shown in Table 2. The differences between this study and other studies are attributed to differing chamber conditions such as light intensity, chamber size and wall-effects, NO_x levels, hydroxyl radical concentrations, and organic mass loading. The organic mass loading ranges from 3 to 483 $\mu\text{g m}^{-3}$ in this study, whereas at organic mass loading $< 50 \mu\text{g m}^{-3}$, the SOA yields are comparable to previous studies. Figure S1 shows that the instantaneous aerosol yield (IAY) trends as: $\text{H}_2\text{O}_2 + \text{low NO}_x > \text{H}_2\text{O}_2 \text{ without NO}_x > \text{high NO}_x \text{ (with HONO)} > \text{low NO}_x$ conditions. The IAY increases with OH radical increasing as well as with increasing reaction rate with OH (k_{OH}). The system reactivity influenced by H_2O_2 , NO_x levels, initial PAH/ NO ratios, NO_2/NO ratios, and all impacted the SOA formation from the PAH precursors. Applying the two-product model (eq(1)) to all naphthalene, 1-methylnaphthalene and 2-methylnaphthalene photooxidation experiments (Figure 1) shows one SOA yield fit curve for the three precursors at higher organic mass loading

range, which indicates the high potential SOA yields among these PAHs. Since the chemical properties such as solid/liquid phase, vapor pressure, and chemical reaction mechanism differ for these three compounds, it was observed that 1-methylnaphthalene presents the highest PAHs precursor that forms the highest SOA yield under similar condition. Overall, the potential PAH SOA precursor yields an order of 1-methylnaphthalene > 2-methylnaphthalene $\approx$ naphthalene.

3.2 Density of SOA evolution

The SOA density measured by the APM-SMPS is displayed as a function of time (Figure 2). The initial SOA densities were $\sim 1.58 \text{ g cm}^{-3}$ for all experiments, decreasing to $\sim 1.3\sim 1.4 \text{ g cm}^{-3}$ and remaining constant during the remainder of the experiment under most conditions, in agreement with a previous aromatic SOA study (Nakao et al., 2013). However, the SOA density decreased continuously for 1-methylnaphthalene photooxidation and 2-merthylnaphthalene under high NO_x conditions (Run ID: 1659A, 1628A, 1623A, 1632A, and 1635A). For these experiments, densities were observed to drop lower than 1 g cm^{-3} , suggesting that the particles are fractal-like (e.g., run 1623A density dropped to 0.7 g cm^{-3}). A power function relationship between effective density and size (equation 4) is used as (Nakao et al., 2011; Park et al., 2003):

$$\rho_{eff} = C d_m^{D_f-3} \quad (4)$$

where ρ_{eff} is the effective density of particles, C is a constant, d_m is the mobility diameter of particles, and D_f is the fractal dimension. D_f is 1 for fractal pattern describing straight chain, D_f is 2 for describing surface sheet, and D_f is 3 for describing spherical particle. For example, the fractal dimension (D_f) in experiment 1623A ranges from 3 to

2.31 over the course of experiment (Figure S4(a)). For these experiments, particle number concentrations of $\sim 10^5$ particles cm^{-3} are observed (Figure S4(b)) yielding a time constant for coagulation in the order of a few hours (Seinfeld and Pandis, 2006). If the SOA is solid, then it is possible that coagulating particles could form such fractal particles for these conditions and timescales with decreasing particle density. Particle density decreased as their mobility diameter increased from 40 nm to 235 nm (Figure S4(a)). Further evidence of fractal 1-methylnaphthalene SOA was observed by injecting *m*-xylene into the chamber at the end of an experiment. The 1-methylnaphthalene SOA density rapidly increased from 1.15 g cm^{-3} to 1.51 g cm^{-3} as liquid *m*-xylene SOA coated the 1-methylnaphthalene SOA filling the fractal voids (Figure S5). Finally, a TEM sample was collected during the 1st hour of particle formation, at 5-6 hours, and at 6-7 hours irradiation time. Figure 2 shows the TEM images collected of SOA formed from 1-methylnaphthalene under high NO_x photooxidation, confirming the formation of fractal SOA particles coagulated after 5~6 hours of photooxidation.

Traditional gas-particle partitioning model usually assume that SOA particles are liquid (Hallquist et al., 2009), but this study presents SOA from 1-methylnaphthalene in environmental chamber can be solid particles with high viscosity under high NO_x condition. This amorphous solid state may influence the partitioning of semi-volatile compounds and inhibit the rate of heterogeneous chemical reactions (Virtanen et al., 2010). Thus, this study challenges traditional views of physical particles phase of SOA formation and demonstrates the importance of measuring density for individual experiments to determine mass based aerosol yield.

350   **3.3 SOA volatility evolution**

351   The volatility trends of strongly decreasing volatility as the experiment progressed were
352   similar for naphthalene, 1-methylnaphthalene and 2-methylnaphthlene photooxidations
353   under high NO_x, H₂O₂ and low NO_x+ H₂O₂ conditions. For example, VRF increased from
354   < 25 % to > 85% (Figure 3(a)) for naphthalene, 1-methylnaphthalene, and 2-
355   methylnaphthalene photooxidation for high-NO_x conditions, even for experiments when
356   the fractal agglomerate formed. This indicates that the vast majority of SOA formed have
357   low volatility even at 100 °C. Additional VTDMA experiments with the thermal denuder
358   temperature set to 150 °C were performed to further explain the volatility of SOA from
359   naphthalene, 1-methylnaphthalene, and 2-methylnaphthalene (Figure 3(b)), while more
360   SOA evaporated at higher temperature, the SOA at the end of the experiment still has a
361   very low volatility (VRF > 60%). The volatility of the SOA was far lower than that
362   measured for monoaromatic compound, such as VRF increased from 18% to 47% for *m*-
363   xylene photooxidation (Qi et al., 2010). These results explained that the low volatility of
364   2-ring PAH photooxidation products undergo condensation, whereas compounds
365   partition from the gas phase 2-ring PAH into the condense phase, that produced
366   extremely low volatility oxidation products (e.g., ring-opening acids, nitronaphthalenes,
367   nitromethylnaphthalenes) with different surface and bulk properties that condense phase
368   reaction can drive the equilibrium towards particle phase and enhance SOA formation.

369   **3.4 Chemical composition characteristics of SOA formation**

370   The HR-ToF-AMS measures the ion fragments from impaction of particles after
371   vaporization on a heated surface (~600 °C) and electron ionization (70 eV) (DeCarlo et

al., 2006). Traces of specific *mass-to-charge* ratios (m/z) are often used to characterize SOA evolution. Numerous studies have used m/z 44 (mostly CO_2^+ , 43.989) associated with carboxylic acids and m/z 43 ($\text{C}_2\text{H}_3\text{O}^+$ (43.018) or C_3H_7^+ (43.054)) associated with oxygenated non-acids (such as aldehydes and ketones) as important indicators of chemical composition and aging of chamber SOA and ambient SOA (e.g., Ng et al., 2010, 2011). The m/z 44 is the key signature of the oxygenated organic compounds formed from PAH SOA formation and the most abundant fragment observed in this study. Typical normalized m/z distributions of naphthalene, 1-methylnaphthalene and 2-methylnaphthalene SOA averaged over the course of the reaction for high- NO_x conditions are shown in Figure 4. The high m/z 44 signal was paired with a high m/z 18 (H_2O^+) peak implying thermal decomposition of the carboxylic acid group at the vaporizer (Alfarra et al., 2004). Additional major ion fragments detected included m/z 43 ($\text{C}_2\text{H}_3\text{O}^+$, 43.018), m/z 50 (C_4H_2^+ , 50.156), m/z 51(C_4H_3^+ , 51.023), the typical aromatics series $\text{C}_6\text{H}_5\text{C}_n\text{H}_{2n}^+$ (m/z 77 (C_6H_5^+ , 77.039), 91(C_7H_7^+ , 91.054), 105 (C_8H_9^+ ,105.070)) (McLafferty and Turecek., 1993), m/z 76 (C_6H_4^+ ,76.031) , m/z 115 (C_9H_7^+ ,115.054), m/z 104 (C_8H_8^+ (104.062) and $\text{C}_7\text{H}_4\text{O}^+$ (104.026)), and m/z 105 ($\text{C}_7\text{H}_5\text{O}^+$ (105.033) and C_8H_9^+ (105.070) isomer). Interestingly, nitro-organic compounds ion fragments were also observed at m/z 131 ($\text{C}_9\text{H}_7\text{O}^+$ (131.049) and $\text{C}_4\text{H}_5\text{NO}_4^+$ (131.021)), m/z 133 ($\text{C}_4\text{H}_7\text{NO}_4^+$ (133.037)) and m/z 145 ($\text{C}_{10}\text{H}_9\text{O}^+$ (145.065) and $\text{C}_5\text{H}_7\text{NO}_4^+$ (145.037)), corresponding to the N-containing compounds like 2-nitrophenol and 4-nitro-1-naphthol observed during OH-initiated naphthalene/high NO_x photooxidation in Kautzman et al (2010) study. The chemical structures of these fragments were proposed and summarized in Table S2.

Three possible PAH photooxidation products are proposed in this study based on a m/z comparison to the NIST library WebBook- *trans*-cinnamic acid, phthalic acid, and benzoic acid (Figure S5). The m/z 147 ($C_9H_7O_2^+$ (147.044)) is the expected major ion fragment of *trans*-cinnamic acid ($C_9H_8O_2$, MW 148) with additional fragments of m/z 148, m/z 103, m/z 77, m/z 51, all present in reasonable ratios in the PAH SOA m/z spectrum. C7 (benzoic acid, etc) and C9 compounds (*trans*-cinnamic acid) are secondary products formed through the O_2 addition to 2-formylcinnamaldehyde to form RO_2 radical that subsequently reacts with NO to form RO radical. It was proposed that loss of CO_2 followed by a hydride shift and oxidation by O_2 and HO_2 would be a possible mechanism to form an acid (Kautzman et al., 2010; Figure S13 scheme 2). Additionally, phthalic acid ($C_8H_6O_4$, M.W. 166) is suggested by the major mass spectrum peak at m/z 104 ($C_7H_4O^+$) along with additional at m/z 76, m/z 18, m/z 50, and m/z 148 (Figure S6, S7). The m/z 104 mass spectra intensity from each high- NO_x PAH experiment shows that the fraction 104 (f_{104}) is 1.82%, 1.14% and 1.28% for naphthalene, 1-methylnaphthalene, and 2-methylnaphthalene, respectively (Figure S8). The mechanisms from the OH oxidation of phthaldialdehyde and further oxidized to form phthalic anhydride and phthalic acid were previously proposed (Figure S14 Scheme 2). Phthalic acid has been identified as major PAH SOA product in previous OH radical-initiated naphthalene reactions (Kautzman et al., 2010; Wang et al., 2007). It is therefore suggested that the m/z 104 can be used as a potential indicator of phthalic acid in HR-ToF-AMS mass spectra distribution from PAH photooxidation. However, because phthalic acid, phthalic anhydride, or phthalic ester can

415 be formed from variety of sources, the m/z 104 use as a marker remains questionable in
416 the ambient measurement.

417 The triangle plot (f_{44} vs. f_{43}) of SOA formation from naphthalene, 1-
418 methylnaphthalene and 2-methylnaphthalene photooxidation for different conditions is
419 shown in Figure S9. The naphthalene SOA lies on the top section of the triangle area, 1-
420 methylnaphthalene SOA sits on the left edge and 2-methylnaphthalene SOA locates on
421 the right edge of the triangle which is known as ambient OOA (Ng et al., 2010). It is
422 suggested that PAHs SOA is highly oxidized since $f_{43} < 0.05$ and the H:C is ~ 1 .
423 Interestingly, f_{43} of 2-methylnaphthalene SOA was much higher than 1-
424 methylnaphthalene and naphthalene, suggesting more aldehydes or ketones (CH_2CHO^+
425 or CH_3CO^+) as well as saturated hydrocarbons (C_3H_7^+) (Alfarra et al., 2004) products are
426 formed from 2-methylnaphthalene than the other PAHs. It suggests that the methyl group
427 on 2-ring PAH impacts OH-initiated oxidation of forming first-generation C11
428 dicarbonyl fragment products (Figure S14 Scheme 3). As determined by Wang et al.
429 (2007), 48% of the OH addition occurs at the C_2 position for 1-methylnaphthalene, and
430 53% of the OH addition occurs at C_1 position for 2-methylnaphthalene, both following
431 the breakage of the C_1 and C_2 bond. Further oxidation of first-generation dicarbonyl
432 fragment product from oxidation of 2-methylnaphthalene was proposed as Figure S15
433 Scheme 4, suggesting more aldehyde group compounds formed with high m/z 43
434 fragment.

435 Under high NO_x conditions, the SOA f_{44} continuously increased from 0.17 to 0.32
436 during naphthalene photooxidation, which is a much larger increase than observed for 1-

437 methylnaphthalene and 2-methylnaphthalene. The same f_{44} aging trend occurs for the
 438 three PAHs precursors under high NO_x , H_2O_2 , and low $\text{NO}_x + \text{H}_2\text{O}_2$ conditions
 439 experiments, indicating that the formation of highly oxidized SOA. Chhabra et al 2010
 440 also reported that higher organic acid concentrations under low- NO_x conditions (H_2O_2
 441 only) from naphthalene oxidation also consistent with the AMS data that characterizes
 442 higher f_{44} values and O/C ratios than those of high- NO_x data, likely due to higher OH
 443 exposures.

444 SOA characteristics including oxygen-to-carbon ratio (O/C), hydrogen-to-carbon ratio
 445 (H/C), and VRF are summarized in Table S1. The average O/C ratios of naphthalene and
 446 methylnaphthalene SOA increased from 0.33 to 0.63 during the course of the experiment.
 447 The H/C ratios for PAH SOA is around 0.9~1.0, which is consistent with Chhabra et
 448 al.(2010) study. The average mean oxidation state of carbon ($\overline{\text{OS}}_c$), calculated as $\overline{\text{OS}}_c \approx$
 449 $2 \text{ O/C} - \text{H/C}$ (Kroll et al., 2011), increases from -0.5 to 0.5 over the course of
 450 experiment. Figure S10 shows the Van Krevelen diagram from PAHs photooxidation for
 451 each of the PAH precursors. The increasing $\overline{\text{OS}}_c$ is consistent with SOA aging during the
 452 course of experiment. The naphthalene and methylnaphthalenes SOA was suggested to be
 453 between low volatility oxygenated OA (LV-OOA) and SV-OOA compared to ambient
 454 OOA in the triangle plot and Van Krevelen diagram as Ng et al. The O/C ratios increased
 455 with irradiation time is consistent with f_{44} formation, which further demonstrated that
 456 oxidized organic aerosol aging property during PAHs photooxidation under both NO_x
 457 conditions and absence of NO_x conditions. It also confirms that the aromaticity of 2-ring

458 PAH allows for multiple oxidation steps through ring opening and bicyclic peroxy radical
459 routes to form more carboxylic acids and hydroperoxides.

460 **4. Conclusions**

461 The characteristics of naphthalene, 1-methylnaphthalene and 2-
462 methylnaphthalene SOA under high NO_x, low NO_x and the absence of NO_x conditions
463 are reported. SOA yields from naphthalene and methylnaphthalene are high with
464 increasing yields of 1-methylnaphthalene > naphthalene ~ 2-methylnaphthalene, differing
465 from the results of earlier studies due to the differences in chamber experimental
466 conditions. The system reactivity influenced by OH radicals, NO_x levels, initial PAH/NO
467 ratios, NO₂/NO ratios, and all impacted the SOA formation from the PAH precursors. It
468 is noted that 1-methylnaphthalene is the highest PAHs precursor that leads to higher SOA
469 potential formation. The CARB emission inventory for toxic shows that naphthalene is
470 the most abundant precursor (910.7 tons/year) among PAHs followed by 2-
471 methylnaphthalene accounting for 81.1 tons/year. Given their high SOA yields, near 1.0,
472 these PAHs can significantly contribute to the aerosol inventory through secondary
473 atmospheric reactions.

474 Further, it was determined that the phase state of 1-methylnaphthalene and 2-
475 methylnaphthalene/high NO_x SOA is solid allowing it to form fractal-like SOA when
476 particle number is high enough to promote coagulation. Formation of fractal SOA
477 particles requires careful evaluation of SOA density to accurately represent SOA mass
478 yields. The *m/z* 104 is identified as a possible indicator of phthalic acid from naphthalene
479 photooxidation by HR-ToF-AMS measurement. Finally, the triangle plot, Van Krevelen

480 diagram, and $\overline{OS}_c$ show significant evolution of the SOA during the course of the
481 experiment.

482

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5. References

- Aiken, A.C., DeCarlo, P.F., Jimenez, J.L., 2007. Elemental analysis of organic species with electron ionization high-resolution mass spectrometry. *Anal. Chem.* 79, 8350–8. doi:10.1021/ac071150w
- Aiken, A.C., Decarlo, P.F., Kroll, J.H., Worsnop, D.R., Huffman, J.A., Docherty, K.S., Ulbrich, I.M., Mohr, C., Kimmel, J.R., Sueper, D., Sun, Y., Zhang, Q., Trimborn, A., Northway, M., Ziemann, P.J., Canagaratna, M.R., Onasch, T.B., Alfarra, M.R., Prevot, A.S.H., Dommen, J., Duplissy, J., Metzger, A., Baltensperger, U., Jimenez, J.L., 2008. O/C and OM/OC ratios of primary, secondary, and ambient organic aerosols with high-resolution time-of-flight aerosol mass spectrometry. *Environ. Sci. Technol.* 42, 4478–4485. doi:10.1021/es703009q
- Aislabie, J., Balks, M., Astori, N., Stevenson, G., Symons, R., 1999. Polycyclic aromatic hydrocarbons in fuel-oil contaminated soils, Antarctica. *Chemosphere* 39, 2201–2207.
- Alfarra, M., Coe, H., Allan, J., Bower, K., Boudries, H., Canagaratna, M., Jimenez, J., Jayne, J., Garforth, a, Li, S., 2004. Characterization of urban and rural organic particulate in the Lower Fraser Valley using two Aerodyne Aerosol Mass Spectrometers. *Atmos. Environ.* 38, 5745–5758. doi:10.1016/j.atmosenv.2004.01.054
- Atkinson, R., Arey, J., 2007. Mechanisms of the Gas-Phase Reactions of Aromatic Hydrocarbons and PAHS with OH and NO₃ Radicals. *Polycycl. Aromat. Compd.* 27, 15–40. doi:10.1080/10406630601134243
- CARB, 2013. California Toxics Inventory “Draft 2010 CTI Summary Table”. Calif. Air Resour. Board. URL <http://www.arb.ca.gov/toxics/cti/cti.htm>
- Carter, W.P.L., CockerIII, D.R., Fitz, D.R., Malkina, I.L., Bumiller, K., Sauer, C.G., Pisano, J.T., Bufalino, C., Song, C., 2005. A new environmental chamber for evaluation of gas-phase chemical mechanisms and secondary aerosol formation. *Atmos. Environ.* 39, 7768–7788. doi:10.1016/j.atmosenv.2005.08.040
- Carter, W.P.L., Luo, D., Malkina, I.L., Pierce, J.A., 1995. Environmental Chamber Studies of Atmospheric Reactivities of Volatile Organic Compounds. Effects of Varying Chamber and Light Source.
- Chan, A.W.H., Kautzman, K.E., Chhabra, P.S., Surratt, J.D., Chan, M.N., Crounse, J.D., Kürten, A., Wennberg, P.O., Flagan, R.C., Seinfeld, J.H., 2009. Secondary organic aerosol formation from photooxidation of naphthalene and alkylnaphthalenes: Implications for oxidation of intermediate volatility organic compounds (IVOCs). *Atmos. Chem. Phys.* 9, 3049–3060. doi:10.5194/acp-9-3049-2009
- Cocker, D.R., Flagan, R.C., Seinfeld, J.H., 2001. State-of-the-art chamber facility for studying atmospheric aerosol chemistry. *Environ. Sci. Technol.* 35, 2594–2601. doi:10.1021/es0019169
- Conde, F.J., Ayala, J.H., Afonso, A.M., González, V., 2005. Emissions of polycyclic aromatic hydrocarbons from combustion of agricultural and sylvicultural debris. *Atmos. Environ.* 39, 6654–6663. doi:10.1016/j.atmosenv.2005.07.043

- DeCarlo, P.F., Kimmel, J.R., Trimborn, A., Northway, M.J., Jayne, J.T., Aiken, A.C., Gonin, M., Fuhrer, K., Horvath, T., Docherty, K.S., Worsnop, D.R., Jimenez, J.L., 2006. Field-deployable, high-resolution, time-of-flight aerosol mass spectrometer. *Anal. Chem.* 78, 8281–8289. doi:10.1021/ac061249n
- Eiguren-Fernandez, A., Miguel, A.H., Froines, J.R., Thurairatnam, S., Avol, E.L., 2004. Seasonal and Spatial Variation of Polycyclic Aromatic Hydrocarbons in Vapor-Phase and PM 2.5 in Southern California Urban and Rural Communities. *Aerosol Sci. Technol.* 38, 447–455. doi:10.1080/02786820490449511
- Grosovsky, A.J., Sasaki, J.C., Arey, J., Eastmond, D.A., Parks, K.K., Atkinson, R., 1999. Evaluation of the potential health effects of the atmospheric reaction products of polycyclic aromatic hydrocarbons. *Res. Rep. Health. Eff. Inst.* i–iv, 1–22; discussion 23–27.
- Hallquist, M., Wenger, J., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N., George, C., Goldstein, A., others, 2009. The formation, properties and impact of secondary organic aerosol: current and emerging issues. *Atmos. Chem. Phys.* 9, 5155–5236.
- Hedberg, E., Kristensson, A., Ohlsson, M., Johansson, C., Johansson, P.Å., Swietlicki, E., Vesely, V., Wideqvist, U., Westerholm, R., 2002. Chemical and physical characterization of emissions from birch wood combustion in a wood stove. *Atmos. Environ.* 36, 4823–4837. doi:10.1016/S1352-2310(02)00417-X
- Hoyle, C.R., Boy, M., Donahue, N.M., Fry, J.L., Glasius, M., Guenther, A., Hallar, A.G., Huff Hartz, K., Petters, M.D., Petäjä, T., Rosenoern, T., Sullivan, A.P., 2011. A review of the anthropogenic influence on biogenic secondary organic aerosol. *Atmos. Chem. Phys.* 11, 321–343. doi:10.5194/acp-11-321-2011
- Jia, C., Batterman, S., 2010. A critical review of naphthalene sources and exposures relevant to indoor and outdoor air. *Int. J. Environ. Res. Public Health* 7, 2903–39. doi:10.3390/ijerph7072903
- Jiang, W., 2003. Instantaneous secondary organic aerosol yields and their comparison with overall aerosol yields for aromatic and biogenic hydrocarbons. *Atmos. Environ.* 37, 5439–5444. doi:10.1016/j.atmosenv.2003.09.018
- Kanakidou, M., Seinfeld, J.H., Pandis, S.N., Barnes, I., Dentener, F.J., Facchini, M.C., Van Dingenen, R., Ervens, B., Nenes, A., Nielsen, C.J., Swietlicki, E., Putaud, J.P., Balkanski, Y., Fuzzi, S., Horth, J., Moortgat, G.K., Winterhalter, R., Myhre, C.E.L., Tsigaridis, K., Vignati, E., Stephanou, E.G., Wilson, J., 2005. Organic aerosol and global climate modelling: a review. *Atmos. Chem. Phys.* 5, 1053–1123. doi:10.5194/acp-5-1053-2005
- Kautzman, K.E., Surratt, J.D., Chan, M.N., Chan, A.W.H., Hersey, S.P., Chhabra, P.S., Dalleska, N.F., Wennberg, P.O., Flagan, R.C., Seinfeld, J.H., 2010b. Chemical composition of gas- and aerosol-phase products from the photooxidation of naphthalene. *J. Phys. Chem. A* 114, 913–34. doi:10.1021/jp908530s
- Kleindienst, T.E., Jaoui, M., Lewandowski, M., Offenberg, J.H., Docherty, K.S., 2012. The formation of SOA and chemical tracer compounds from the photooxidation of naphthalene and its methyl analogs in the presence and absence of nitrogen oxides. *Atmos. Chem. Phys. Discuss.* 12, 12163–12201. doi:10.5194/acpd-12-12163-2012

- Kroll, J., Donahue, N., Jimenez, J., 2011. Carbon oxidation state as a metric for describing the chemistry of atmospheric organic aerosol. *Nat. Chem.* 3, 133–139. doi:10.1038/nchem.948
- Kroll, J.H., Seinfeld, J.H., 2008. Chemistry of secondary organic aerosol: Formation and evolution of low-volatility organics in the atmosphere. *Atmos. Environ.* 42, 3593–3624. doi:10.1016/j.atmosenv.2008.01.003
- Lewtas, J., 2007. Air pollution combustion emissions: characterization of causative agents and mechanisms associated with cancer, reproductive, and cardiovascular effects. *Mutat. Res.* 636, 95–133. doi:10.1016/j.mrrev.2007.08.003
- Lin, C.Y., Wheelock, A.M., Morin, D., Baldwin, R.M., Lee, M.G., Taff, A., Plopper, C., Buckpitt, A., Rohde, A., 2009. Toxicity and metabolism of methylnaphthalenes: comparison with naphthalene and 1-nitronaphthalene. *Toxicology* 260, 16–27. doi:10.1016/j.tox.2009.03.002
- Loza, C.L., Chan, A.W.H., Galloway, M.M., Keutsch, F.N., Flagan, R.C., Seinfeld, J.H., 2010. Characterization of vapor wall loss in laboratory chambers. *Environ. Sci. Technol.* 44, 5074–8. doi:10.1021/es100727v
- Lu, R., Wu, J., Turco, R.P., Winer, A.M., Atkinson, R., Arey, J., Paulson, S.E., Lurmann, F.W., Miguel, A.H., Eiguren-Fernandez, A., 2005. Naphthalene distributions and human exposure in Southern California. *Atmos. Environ.* 39, 489–507. doi:10.1016/j.atmosenv.2004.09.045
- Malloy, Q.G.J., Nakao, S., Qi, L., Austin, R., Stothers, C., Hagino, H., Cocker, D.R., 2009. Real-Time Aerosol Density Determination Utilizing a Modified Scanning Mobility Particle Sizer—Aerosol Particle Mass Analyzer System. *Aerosol Sci. Technol.* 43, 673–678. doi:10.1080/02786820902832960
- McDonald, J.D., Zielinska, B., Fujita, E.M., Sagebiel, J.C., Chow, J.C., Watson, J.G., 2003. Emissions from charbroiling and grilling of chicken and beef. *J. Air Waste Manag. Assoc.* 53, 185–194. doi:10.1080/10473289.2003.10466141
- McLafferty, F.W., Turecek, F., 1993. Interpretation of mass spectra. University Science Books, Sausalito, California. doi:10.1002/bms.1200230614
- Nakao, S., Liu, Y., Tang, P., Chen, C.-L., Zhang, J., Cocker III, D.R., 2012. Chamber studies of SOA formation from aromatic hydrocarbons: observation of limited glyoxal uptake. *Atmos. Chem. Phys.* 12, 3927–3937. doi:10.5194/acp-12-3927-2012
- Nakao, S., Shrivastava, M., Nguyen, A., Jung, H., Cocker, D., 2011. Interpretation of Secondary Organic Aerosol Formation from Diesel Exhaust Photooxidation in an Environmental Chamber. *Aerosol Sci. Technol.* 45, 964–972. doi:10.1080/02786826.2011.573510
- Nakao, S., Tang, P., Tang, X., Clark, C.H., Qi, L., Seo, E., Asa-Awuku, A., Cocker, D., 2013. Density and elemental ratios of secondary organic aerosol: Application of a density prediction method. *Atmos. Environ.* 68, 273–277. doi:10.1016/j.atmosenv.2012.11.006
- Ng, N.L., Canagaratna, M.R., Jimenez, J.L., Chhabra, P.S., Seinfeld, J.H., Worsnop, D.R., 2011. Changes in organic aerosol composition with aging inferred from aerosol mass spectra. *Atmos. Chem. Phys.* 11, 6465–6474. doi:10.5194/acp-11-6465-2011

- Ng, N.L., Canagaratna, M.R., Zhang, Q., Jimenez, J.L., Tian, J., Ulbrich, I.M., Kroll, J.H., Docherty, K.S., Chhabra, P.S., Bahreini, R., Murphy, S.M., Seinfeld, J.H., Hildebrandt, L., Donahue, N.M., DeCarlo, P.F., Lanz, V.A., Prévôt, A.S.H., Dinar, E., Rudich, Y., Worsnop, D.R., 2010. Organic aerosol components observed in Northern Hemispheric datasets from Aerosol Mass Spectrometry. *Atmos. Chem. Phys.* 10, 4625–4641. doi:10.5194/acp-10-4625-2010
- Nishino, N., Arey, J., Atkinson, R., 2012. 2-Formylcinnamaldehyde formation yield from the OH radical-initiated reaction of naphthalene: effect of NO(2) concentration. *Environ. Sci. Technol.* 46, 8198–204. doi:10.1021/es301865t
- Nishino, N., Arey, J., Atkinson, R., 2009. Yields of glyoxal and ring-cleavage co-products from the OH radical-initiated reactions of naphthalene and selected alkyl naphthalenes. *Environ. Sci. Technol.* 43, 8554–60. doi:10.1021/es902018v
- Park, K., Cao, F., Kittelson, D.B., McMurry, P.H., 2003. Relationship between particle mass and mobility for diesel exhaust particles. *Environ. Sci. Technol.* 37, 577–83.
- Pye, H.O.T., Pouliot, G. A., 2012. Modeling the role of alkanes, polycyclic aromatic hydrocarbons, and their oligomers in secondary organic aerosol formation. *Environ. Sci. Technol.* 46, 6041–7. doi:10.1021/es300409w
- Qi, L., Nakao, S., Malloy, Q., Warren, B., Cocker III, D.R., 2010. Can secondary organic aerosol formed in an atmospheric simulation chamber continuously age? *Atmos. Environ.* 44, 2990–2996. doi:10.1016/j.atmosenv.2010.05.020
- Qi, L., Nakao, S., Tang, P., Cocker III, D.R., 2010. Temperature effect on physical and chemical properties of secondary organic aerosol from *m*-xylene photooxidation. *Atmos. Chem. Phys. Discuss.* 10, 863–883. doi:10.5194/acpd-10-863-2010
- Rader, D.J., McMurry, P.H., 1986. Application of the tandem differential mobility analyzer to studies of droplet growth or evaporation. *J. Aerosol Sci.* doi:10.1016/0021-8502(86)90031-5
- Reisen, F., Arey, J., 2005. Atmospheric Reactions Influence Seasonal PAH and Nitro-PAH Concentrations in the Los Angeles Basin. *Environ. Sci. Technol.* 39, 64–73. doi:10.1021/es035454l
- Sasaki, J., Aschmann, S.M., Kwok, E.S.C., Atkinson, R., Arey, J., 1997. Products of the Gas-Phase OH and NO₃ Radical-Initiated Reactions of Naphthalene. *Environ. Sci. Technol.* 31, 3173–3179. doi:10.1021/es9701523
- Schulz, M., Textor, C., Kinne, S., Balkanski, Y., Bauer, S., Berntsen, T., Berglen, T., Boucher, O., Dentener, F., Guibert, S., Isaksen, I.S. a., Iversen, T., Koch, D., Kirkevåg, A., Liu, X., Montanaro, V., Myhre, G., Penner, J.E., Pitari, G., Reddy, S., Seland, Ø., Stier, P., Takemura, T., 2006. Radiative forcing by aerosols as derived from the AeroCom present-day and pre-industrial simulations. *Atmos. Chem. Phys.* 6, 5225–5246. doi:10.5194/acp-6-5225-2006
- Seinfeld, J.H., Pandis, S.N., 2006. *Atmospheric Chemistry and Physics : From Air Pollution to Climate Change* (2nd Edition). John Wiley & Sons, Somerset, NJ, USA.
- Shah, S.D., Ogunyoku, T. A, Miller, J.W., Cocker, D.R., 2005. On-road emission rates of PAH and n-alkane compounds from heavy-duty diesel vehicles. *Environ. Sci. Technol.* 39, 5276–84. doi:10.1021/es048086+
- Shakya, K.M., Griffin, R.J., 2010. Secondary organic aerosol from photooxidation of

- polycyclic aromatic hydrocarbons. *Environ. Sci. Technol.* 44, 8134–9. doi:10.1021/es1019417
- Tang, P., Nakao, S., Qi, L., Chen, C.-L., Cocker III, D.R., 2015. Role of Alkyl substituents on Secondary Organic Aerosol Formation from Aromatic Hydrocarbons: Part-II Chemical Composition.
- Virtanen, A., Joutsensaari, J., Koop, T., Kannosto, J., Yli-Pirilä, P., Leskinen, J., Mäkelä, J.M., Holopainen, J.K., Pöschl, U., Kulmala, M., Worsnop, D.R., Laaksonen, A., 2010. An amorphous solid state of biogenic secondary organic aerosol particles. *Nature* 467, 824–7. doi:10.1038/nature09455
- Wang, L., Atkinson, R., Arey, J., 2007. Dicarbonyl products of the OH radical-initiated reactions of naphthalene and the C1- and C2-alkylnaphthalenes. *Environ. Sci. Technol.* 41, 2803–2810. doi:10.1021/es0628102

6. Tables and Figures

Table 1 Initial experimental conditions and SOA yield for all experiments

High-NO _x (with HONO)		HC ₀	ΔHC	NO ^a	NO ₂ ^a	NO ^b	NO ₂ ^b	ΔM ₀	SOA yield ^c	Density
Run ID	Compound	ppb	μg/m ³	ppb	ppb	ppb	ppb	μg/m ³		g/cm ³
1586A	naphthalene	45.3	168	73	94	510	188	94.8	0.60	1.48 ^d
1588A	naphthalene	29.1	126	N.D.	104	610	166	59.4	0.47	1.48 ^d
1590A	naphthalene	25.9	116	20	142	420	338	47.1	0.41	1.47
1732A	naphthalene	29.6	105	25	38	624	152	3.0	0.03	1.51
1737A	naphthalene	22.6	80	50	88	576	207	20.3	0.25	1.40
1623A	1-methylnaphthalene	67.7	362	44	177	396	440	375.2	1.04	0.92 (1.47→0.71)
1628A	1-methylnaphthalene	40.0	203	26	103	397	372	173.7	0.78	1.07 (1.49→0.83)
1652A	1-methylnaphthalene	14.2	52	68	50	476	284	10.4	0.21	1.25 ^e
1659A	1-methylnaphthalene	26.8	111	63	81	445	341	74.1	0.65	1.25 (1.54→1.06)
1770A	1-methylnaphthalene	47.0	253	294	202	400	216	383.2	1.52	1.23 (1.48→1.12)
1632A	2-methylnaphthalene	30.6	148	28	77	380	321	51.1	0.35	1.32
1635A	2-methylnaphthalene	41.2	211	47	83	403	348	89.7	0.43	1.26
1768A	2-methylnaphthalene	47.7	182	145	104	530	168	61.1	0.34	1.35
1775A	2-methylnaphthalene	43.7	163	148	117	515	145	89.1	0.55	1.32
Low NO _x condition		HC ₀	ΔHC	NO ^a	AS ^g seed(μm ³ /cm ³)		ΔM ₀	Y	Density	
1592A	naphthalene	28.0	135	22			5.7	0.04	1.48	
1660A	naphthalene + AS	17.1	86	14	17.3		15.5	0.18	1.58	
1661A	naphthalene	14.7	76	13			21.1	0.28	1.47	
1668A	naphthalene + AS	15.9	77	21	41.9		9.7	0.13	1.61	
1718A	naphthalene	27.1	140	19			30.8	0.22	1.48	
1828A	naphthalene	34.7	173	10			50.1	0.29	1.48 ^d	
1992A	naphthalene + AS	27.0	125	18	15.4		34.5	0.28	1.58	
1992B	naphthalene	28.7	142	18			27.1	0.19	1.48	
2040A	naphthalene + AS	14.6	69	10	3.4		22.7	0.33	1.48	
2040B	naphthalene	16.9	84	11			26.2	0.31	1.48 ^d	
1616A	1-methylnaphthalene	34.8	114	63			18.7	0.14	1.41	
1616B	1-methylnaphthalene	35.0	185	29			34.8	0.19	1.4 ^f	
1742A	1-methylnaphthalene	45.3	218	71			44.1	0.20	1.44	
1664A	1-methylnaphthalene	25.9	148	13			107.0	0.72	1.40	
1666A	2-methylnaphthalene	20.0	115	12			56.3	0.49	1.37	
1744A	2-methylnaphthalene	26.4	152	49			8.5	0.06	1.40	
1745A	2-methylnaphthalene	29.1	157	13			43.4	0.28	1.33	
H ₂ O ₂ / H ₂ O ₂ +low NO _x conditions				NO ^a	H ₂ O ₂ (ppm)		ΔM ₀	Y	Density	
1584A	naphthalene	24.6	114	-	2		68.5	0.62	1.48 ^d	
1585A	naphthalene	48.0	313	-	2		201.0	0.96	1.48 ^d	
1754A	naphthalene	20.8	100	-	1		87.4	0.58	1.48 ^d	
1776A	naphthalene	46.5	207	-	1		190.3	0.95	1.49	
1596A	1-methylnaphthalene	35.6	201	-	1		234.5	1.19	1.4 ^f	
1598A	1-methylnaphthalene	24.8	139	-	1		164.9	1.19	1.4 ^f	
1600A	1-methylnaphthalene	50.7	274	-	1		483.2	1.81	1.37	
1608A	2-methylnaphthalene	28.6	162	-	1		128.7	0.81	1.39	
1772A	2-methylnaphthalene	40.9	232	-	1		202.8	0.87	1.37	
1613A	naphthalene	34.8	181	59	1		208.3	1.15	1.43	
1650A	1-methylnaphthalene	36.6	209	38	1		403.4	1.93	1.26(1.49→1.05)	
1643A	2-methylnaphthalene	34.0	195	55	1		246.5	1.26	1.30	

a: initial NO and NO₂ concentration when injecting HONO; b: initial NO and NO₂ concentration after injecting additional NO and mixing reactors before turning blacklights on; c : SOA yield is calculated at the end of each experiment. Each experiment irradiates for 6 to 8 hours. d: assume average density of naphthalene SOA is 1.48 g/cm³.e: assume average density of 1-methylnaphthalene high NO_x SOA is 1.25 g/cm³; f: assume density of 1-methylnaphthalene H₂O₂+ low NO_x SOA is 1.4 g/cm³; g: AS: ammonium sulfate.

Table 2 Comparison of SOA yield from PAHs photooxidation

PAHs	Condition	SOA yield (Chan et al., 2009) ^a	SOA yield (Kleindienst et al., 2012) ^b	SOA yield (Shakya and Griffin, 2010) ^d	SOA yield (this study)
naphthalene	high NO _x	0.19~0.30	0.28 ^c	0.08~0.16	0.03~0.60
naphthalene	low NO _x +H ₂ O ₂	0.73	---	---	1.15
naphthalene	low NO _x	---	---	---	0.04~0.33
naphthalene	H ₂ O ₂	---	0.18-0.36	---	0.58~0.96
1-methylnaphthalene	high NO _x	0.19~0.39	0.20	0.03-0.22	0.21~1.52
1-methylnaphthalene	low NO _x +H ₂ O ₂	0.68	0.41	---	1.93
1-methylnaphthalene	H ₂ O ₂	---	---	---	1.19~1.81
1-methylnaphthalene	low NO _x	---	---	---	0.14~0.72
2-methylnaphthalene	high NO _x	0.26~0.45	0.15	0.04-0.13	0.34~0.55
2-methylnaphthalene	low NO _x +H ₂ O ₂	0.58	0.64	---	1.26
2-methylnaphthalene	H ₂ O ₂	---	---	---	0.81~0.87
2-methylnaphthalene	low NO _x	---	---	---	0.06~0.49

a: aerosol mass loadings (ΔM_0) : 10~40 $\mu\text{g}/\text{m}^3$; b: aerosol mass loadings (ΔM_0) : 39~130 $\mu\text{g}/\text{m}^3$; c: 0.14ppm CH₃ONO, 300 ppb NO for ΔM_0 100 $\mu\text{g}/\text{cm}^3$; d: aerosol mass loadings (ΔM_0) : 4~18 $\mu\text{g}/\text{m}^3$.

Figure 1 Two-product model curve for SOA yield from naphthalene, 1-methylnaphthalene and 2-methylnaphthalene photooxidation. Coefficients of α_1 , $K_{om,1}$, α_2 , $K_{om,2}$ are 0.9880, 0.0014, 2.2153, and 0.0030.

Figure 2 Time series of the densities of SOA from naphthalene, 1-methylnaphthalene and 2-methylnaphthalene photooxidation under different conditions.

Figure 3 Volume remaining fraction (VRF) evolution of SOA during the courses of experiments under (a) high NO_x, H₂O₂, low NO_x and H₂O₂ conditions at thermodenuder temperature of 100 °C, (b) high NO_x conditions at 150 °C, (c) low NO_x conditions at 150 °C.

(a) 1629A Naphthalene/high-NO_x

(b) 1628A 1-Methylnaphthalene/high-NO_x

(c) 1768A 2-Methylnaphthalene/high-NO_x

Figure 4 Normalized HR-ToF-AMS mass spectra distribution of three representative high-NO_x SOA experiments. (a) naphthalene high-NO_x; (b) 1-methylnaphthalene high-NO_x; (c) 2-methylnaphthalene high-NO_x. (see also Figure S2.10-S2.12)