Lawrence Berkeley National Laboratory

Lawrence Berkeley National Laboratory

Title

Sampling Artifacts from Conductive Silicone Tubing

Permalink

https://escholarship.org/uc/item/9z39j8qz

Author Timko, Michael T.

Publication Date 2009-06-18

1	Sampling Artifacts from Conductive Silicone Tubing
2 3	A manuscript submitted to Aerosol Science & Technology
4	
5 6	Michael T. Timko*, Zhenhong Yu, Jesse Kroll, John T. Jayne, Douglas R. Worsnop Richard C. Miake-Lye, and Timothy B. Onasch
7	Center for Acro Thermodynamics and Center for Acrossland Cloud Chemistry
0 0	Aerodyne Research Inc
10	45 Manning Road, Billerica MA 01821-3976
11	978.663.9500, timko@aerodyne.com
12	
13	David Liscinsky
14	Combustion Group
15	United Technologies Research Center
16	
17	Thomas W. Kirchstetter and Hugo Destaillats
18	Environmental Energy Technologies Division
19	Lawrence Berkeley National Laboratory, Berkeley, California 94720
20	Amora I. Halden
21	Amara L. Holder
22 22	Environmental Health Sciences University of California Barkeley, Barkeley, California 04720
$\frac{23}{24}$	University of Camorina-Derkeley, Derkeley, Camorina 94720
2 - 25	Iared D. Smith and Kevin R. Wilson
26	Chemical Sciences Division
27	Lawrence Berkeley National Laboratory
28	1 Cyclotron Road Mail Stop 6R2100
29	Berkeley, CA 94720-8226
30	
31	Abstract. We report evidence that carbon impregnated conductive silicone tubing used in
32	aerosol sampling systems can introduce two types of experimental artifacts: 1) silicon
33	tubing dynamically absorbs carbon dioxide gas, requiring greater than 5 minutes to reach
34	equilibrium and 2) silicone tubing emits organic contaminants containing siloxane that
35	adsorb onto particles traveling through it and onto downstream quartz fiber filters. The
36	consequence can be substantial for engine exhaust measurements as both artifacts directly
37	impact calculations of particulate mass-based emission indices. The emission of
38	contaminants from the silicone tubing can result in overestimation of organic particle

Sampling Artifacts from Conductive Silicone Tubing

4/10/2009

39	mass concentrations based on real-time aerosol mass spectrometry and the off-line
40	thermal analysis of quartz filters. The adsorption of siloxane contaminants can affect the
41	surface properties of aerosol particles; we observed a marked reduction in the water-
42	affinity of soot particles passed through conductive silicone tubing. These combined
43	observations suggest that the silicone tubing artifacts may have wide consequence for the
44	aerosol community and should, therefore, be used with caution. Contamination
45	associated with the use of silicone tubing was observed at ambient temperature and, in
46	some cases, was enhanced by mild heating (<70 $^{\circ}$ C) or pre-exposure to a solvent
47	(methanol). Further evaluation is warranted to quantify systematically how the
48	contamination responds to variations in system temperature, physicochemical particle
49	properties, exposure to solvent, sample contact time, tubing age, and sample flow rates.
50	
51	1. Introduction. Typical aerosol characterization experiments require tubing to convey
52	particle-laden gas streams from the source to the particle characterization instruments.
53	Aircraft gas turbine engine exhaust gas – which must be cooled and diluted prior to
54	reaching the instruments – is a specific particle source which nearly always requires use
55	of sample extraction and sample tubing (Lobo et al., 2007). Even most studies of
56	ambient particles require a short length (< 3m) of tubing to convey and distribute sample
57	to particle instruments. To avoid experimental bias, sample tubing must meet the
58	following two requirements: 1) high particle transmission efficiency (as close to 100% as
59	possible) for particles of all important sizes; 2) zero particle contamination (including
60	condensation and/or nucleation).

61	Several monographs describe the guidelines for minimizing particle losses in
62	sample probes and sample lines (Brockman, 1993; Hinds, 1999). Kumar et al. (2008)
63	recently reported results and comparison with theory for a line-loss study directed at
64	quantifying the particle loss effects encountered in street canyon experiments. The most
65	prevalent mechanisms for particle loss include diffusional loss, inertial loss, and
66	electrostatic loss. For particles relevant to engine exhaust studies (3-300 nm diameter),
67	diffusional and inertial losses are minimized by maintaining turbulent flow, employing
68	sample tubes with large volume/surface area ratio, maintaining short residence times, and
69	avoiding sharp bends. Electrostatic losses are eliminated by use of conductive tubing
70	which prevents localized build-up of charge on the tube walls. Metals (copper,
71	aluminum, stainless steel) are the preferred materials for particle sampling tubing. In
72	some applications, flexible tubing may be desired – especially in cases where rapid setup
73	is required, for translating sample probe systems, or if the sampling system requires
74	connections be made in tight spaces.
75	Recent use of carbon impregnated conductive silicone tubing as a flexible
76	alternative to metal tubing has become prevalent. Several vendors supply silicone tubing
77	and we have found no substantive variation in the performance of their products.
78	Compared to metal tubing, conductive silicone tubing can be assembled rapidly and made
79	to conform to unusual space requirements. Based on particle transmission alone,
80	conductive silicone tubing is an acceptable substitute to metal. Figure 1 shows that
81	particle transmission through conductive silicone tubing is nearly equal to that for
82	stainless steel tubes, all other variables held nearly constant (50 m of tubing flowing
83	particle laden gas at 50 SLPM, 297.4 K, 1 bar, 1.75 cm i.d. for silicone tubing, 1.17 cm





85 Figure 1. Fractional penetration (transmission) of size selected soot particles through test sections of stainless steel, conductive silicone, and polyvinyl chloride tubing. Fractional 86 penetration is nearly identical for stainless steel, and conductive silicone tubing. 87 88 Electrostatic losses in the non-conducting polyvinyl chloride tubing greatly reduce 89 particle transmission. The penetration calculated for conductive tubing is shown for 90 reference. Calculated penetration includes losses due to diffusion and inertia (settling), 91 but not electrostatic losses. Conditions: 50 SLPM flow rate, 1.27 cm i.d. tubing, 50m 92 tubing length, 25°C, 1 bar pressure.

95 i.d. for stainless steel tubing). For the conductive silicone and stainless steel tubing,

96 penetration is greater than 90% for particles between about 50 and 200 nm and drops

97 rapidly for particles smaller than 50 nm. The predicted penetration agrees exceptionally

98 well with that observed for all particle sizes considered, provided that the tubing is

- 99 conductive. The much lower particle penetration shown in Figure 1 for polyvinyl
- 100 chloride (PVC) tubing is likely due to electrostatic losses. Typical application of
- 101 conductive silicone tubing for particle counting measurements (e.g. condensation particle

102 counters (CPC), scanning mobility particle sizers (SMPS), and kindred instruments) may103 be justified.

104

105 2. Sampling Artifacts. Despite being appropriate for certain applications, we 106 recommend that silicone tubing be used judiciously. We have identified two sampling 107 artifacts that conductive silicone tubing introduces: 1) biases in sampled carbon dioxide 108 concentrations, and 2) emission of siloxane compounds that contaminate air and particles 109 transported through the tubing. We share laboratory and field data which provide 110 evidence of both types of artifacts. The carbon dioxide artifact can cause miscalculation 111 of sample dilution and pollutant emission indices (mass pollutant emitted per mass of fuel 112 consumed) for engine exhaust studies. The siloxane artifact alters particle composition, 113 inflates particle mass (especially mass of semi-volatile particles), changes particle surface 114 properties, and introduces positive mass biases into filter-based sampling methods for 115 particulate carbon. Table 1 summarizes our findings and respective conditions. When 116 combined with the findings of other reports (Yu, 2009 and Schneider et al., 2006), a 117 sufficient body of experimental evidence exists to warrant caution when using silicone 118 tubing for aerosol sampling and characterization experiments, especially since standard 119 testing procedures may not reveal the contamination.

120Artifact 1: Carbon Dioxide Uptake. For engine exhaust measurements, above ambient121levels of CO_2 are taken as tracers for fuel combustion. Uptake of CO_2 into silicone122tubing will introduce errors in the calculation of the dilution ratio used to quantify the123mass of pollutant release per unit fuel burned (emission indices). To quantify the uptake124effect, the concentration of CO_2 was measured before and after passing through test

125

Particle source	Sample Temp ^a (°C)	L (m)	i.d. (cm)	t _{res} (sec)	Observation	Description in text
filtered air	24.3	15.2	1.75		~5% CO ₂ uptake into tubing	Fig. 2
filtered air	22 and 45	0.75	1.1	0.5	gaseous organic carbon sorbed onto downstream quartz filters	Fig. 7
filtered air	20-25	0.3	0.64	0.2	PDMS particle entrainment <50 ng m ⁻³	Section 4. Mechanisms of Siloxane Uptake by Particles
ambient sulfate particles	20-25	~1	0.64	0.02	<0.1 wt% uptake of PDMS	Section 4. Mechanisms of Siloxane Uptake by Particles
gas turbine engine lubrication oil	<70 ^b	~1	0.64	0.02	<2 wt% uptake of PDMS onto particles	Section 4. Mechanisms of Siloxane Uptake by Particles
gas turbine engine lubrication oil	20-25	0.3	0.64	0.2	1-2 wt% uptake of PDMS onto particles	Section 4. Mechanisms of Siloxane Uptake by Particles
organic PM in laboratory air ^c	20-25	0.3	0.64	0.2	1-3 wt% uptake onto particles	Fig. 4
atomized squalane ^d particles	20-25	1	0.64	1.5	conclusive identification of PDMS using VUV ionization and high resolution mass spectrometry	Fig. 5
gas turbine engine soot	<70 ^b	~1	0.64	0.02	identification of PDMS contaminant 30 wt% uptake of PDMS onto particles	Fig. 3 Consequence 1: Addition of Particle Mass
diffusion	20-25	0.3	0.64	0.2	10 wt% onto particles	Fig. 4
diffusion flame soot	22 and 51	0.75	1.1	0.5	PDMS detected on particles using FTIR	Fig. 6
diffusion flame soot	22 and 45	0.75	1.1	0.5	reduced soot's water affinity	Fig. 8

Table. Summary of Silicone Tubing Observations

^a air temperature inside tubing at its heated inlet (i.e., maximum temperature)

^b estimated based on exhaust gas temperature of 900 °C and 20:1 dilution with 30 °C
 nitrogen

129 c air found in the Aerodyne Research, Inc. laboratory space contained organic particles,

which under un-controlled conditions, picked up PDMS from the conductive siliconetubing

^d tubing expose to methanol prior to observation of PDMS contamination of particles

133	sections of flexible conductive silicone (1.75 cm i.d. x 15.2 m) and rigid 306 stainless
134	steel tubing (1.17 cm i.d. x 15.2 m). The sample lengths used here are typical for engine
135	exhaust experiments which require a substantial standoff distance between the engine and
136	the test equipment, as is the case for testing of gas turbine engine exhaust. Flow rates of
137	5 and 50 SLPM were used giving residence times of ~40 and 4 seconds. Three CO_2
138	concentrations characteristic of engine exhaust were tested (5.00%, 1.69% and 0.80%).
139	In a typical experiment, the test section of tubing was conditioned by flowing CO ₂ -free
140	nitrogen gas over it for roughly 10 min. Then, CO ₂ was introduced into the stream at the
141	desired mixing ratio and fed directly to the CO ₂ detector, bypassing the test section. The
142	CO_2 gas was then re-directed to the test section of tubing and the CO_2 concentration
143	monitored. Figure 2 shows representative CO ₂ data collected after passing through the
144	stainless steel and silicone test sections. Data are normalized using the CO_2
145	concentration measured in bypass mode. Compared to stainless steel, the CO_2
146	concentration was reduced by ~5% (from 50,000 ppm to 47,500 ppm) after passing
147	through the silicone tubing. Similar decreases in CO ₂ concentrations were observed at
148	the lower CO_2 concentrations tested. The CO_2 concentrations appeared to recover with
149	time; however, they did not fully recover after 5 min of stable operation. For many
150	experiments (e.g., transient exhaust plume sampling or when engine test time is limited),
151	the transient uptake of CO_2 may introduce systematic errors on the order of 5% in CO_2
152	concentration and emission index calculations - or require careful planning of test
153	conditions and substantial (> 5 min) equilibration times. Tubing lengths shorter than 15.2
154	m had smaller fractional CO ₂ uptake, and the system returned to 100% CO ₂ transmission





Figure 2. CO_2 concentrations in air dilution gas (initially 50,000 ppm CO_2) directly from the flow manifold and after transport through 15.2 m of stainless steel or 15.2 m of conductive silicone tubing. The CO_2 concentration is about 5% lower after transport through silicone tubing as compared to its concentration direct from the manifold or after transport through stainless steel tubing. The CO_2 concentration after transmission through silicone tubing appears to slowly recover, but the dynamic response time is greater than 5 min.

164 more rapidly than shown in Figure 2, indicating that the CO₂ absorption effect might be

165 minimized using short lengths of silicone tubing.

166

167 Artifact 2: Emission of Siloxanes. We have seen evidence of contamination emitted

168 from the silicone tubing used for several different research applications and have

169 identified siloxanes as the key constituent of the contamination using independent

analytical techniques.

171 We previously observed siloxane compounds during several campaigns to

172 characterize aircraft engine exhaust particles (APEX-1, Lobo et al., 2007, Onasch et al.,

2008; JETS-APEX2/APEX3, Timko et al., 2009). With repeated observation, we grew 173 174 suspicious that the source of the siloxanes may not be aircraft related. We have now 175 accumulated data from three separate sources that confirm that silicone tubing is the 176 source of the siloxane contamination: 1) 70 eV electron impact (EI) ionization aerosol 177 mass spectrometry of gas turbine engine soot particles and laboratory jet fuel diffusion 178 flame soot, 2) VUV-ionization high-resolution aerosol mass spectrometry of organic 179 particles, and 3) Fourier transform infrared (FTIR) spectroscopy of diffusion flame soot 180 particles collected on quartz filters. 181 Although we had detected trace siloxane during previous aviation experiments, 182 these events provided too little signal (<5% of the total organic PM) to perform a 183 rigorous chemical analysis. A more recent engine test (Timko et al., 2009) provided 184 sufficient data to make a positive identification. Figure 3a shows a characteristic mass 185 spectrum (m/z 40-300) of the engine exhaust particles obtained by an aerosol mass 186 spectrometer (Jayne et al., 2000; Canagaratna et al., 2007). During that test, the majority 187 (20 m) of tubing was stainless steel or copper, with two important exceptions: 1) several 188 short sections (1m total length) of silicone tubing were used in a valve box designed to 189 distribute gases to various experimental groups and 2) two short pieces (1m total length) 190 of 0.51 cm i.d. conductive siloxane tubing were used to make several tight connections 2 191 m before the sample gas reached the particle characterization instruments. Due to its 192 proximity to the engine, the tubing in the valve box may have been exposed to elevated 193 temperatures (T < 70 °C) during the test. Though the exact temperature at that location 194 was never measured, we estimated an upper limit. We assumed that the maximum 195 exhaust gas temperature was 900 °C, consistent with data from a recent field



Figure 3. Characteristic EI ionization mass spectra obtained for a) engine exhaust particles and b) aerosolized polydimethylsiloxane (PDMS). The m/z features distinctive of PDMS, (m/z = 73, 147, 207, 221, 281) are readily apparent as a contaminant in the engine exhaust particles.

202 measurements (Wey et al., 2006). Prior to the sample reaching the silicone tubing, the

raw exhaust gas was diluted by a factor of at least 20 using dry nitrogen at 30 °C.

204 Assuming similar heat capacities for nitrogen and the exhaust gas (which is an accurate

simplication), the estimated gas temperature contacting the silicone tubing was 70 °C.

206 Since we took an upper limit on the initial exhaust gas temperature and since heat transfer

- 207 with the surroundings would further reduce the final temperature, we assign 70 °C as the
- 208 upper limit for the gas when it contacted the silicone tubing during the gas turbine
- 209 exhaust experiments.

210	The spectrum in Figure 3a was measured for particles sampled 1 m from the exit
211	nozzle of a commercial gas turbine engine operating at 85% of its full rated thrust.
212	Electron impact (EI), a technique associated with significant molecular fragmentation,
213	was the ionization method for the spectra in Figure 3, and the resolution was unit mass
214	(m/ Δ m \approx 800 at m/z 184). In addition to features consistent with fragmentation of a
215	hydrocarbon backbone (m/z = 41, 43, 55, 57, etc.), a series of lines with m/z = 73, 147,
216	207, 221, and 281 is clearly evident in the mass spectrum. The distinctive m/z pattern
217	allows identification of an organosilicon compound in the particles.
218	Dong et al. (1998) recorded the time-of-flight secondary ion mass spectra (ToF-
219	SIMS) of several organosilicon polymers using gas chromatography tandem mass
220	spectrometry. Dong et al. (1998) report that the $[nR + 73]^+$ fragment is a common feature
221	of siloxanes. Of the silicon-bearing polymers tested by Dong et al. (1998),
222	polydimethylsiloxane (PDMS) provided the best match to the field spectrum shown in
223	Figure 3a. Schneider et al. (2006) observed the m/z 147, 221, 295 series during aerosol
224	mass spectrometer characterization of soot particles that had passed through a short
225	(unspecified) length of conductive silicone tubing and assigned the spectra features to
226	$[(SiOC_2H_6)_n(SIOC_2H_5)]^+$ (with $n = 1, 2, and 3$). Yu et al. (2009) found a siloxane
227	contaminant on NaNO ₃ particles that had contacted conductive silicone tubing. Yu et al
228	(2009) used high resolution electron impact ionization to assign the m/z 147, 221, 295,
229	369 series to $[(SiOC_2H_6)_nSi(CH_3)_3]^+$ (with $n = 1, 2, 3, 4$) and the m/z 207, 281, 355, 429
230	series to $[(SiOC_2H_6)_n(SiOCH_3)]^+$ (with $n = 2, 3, 4, 5$).
231	We confirmed the PDMS assignment by performing a laboratory test. Figure 3b
232	shows the mass spectrum of a PDMS sample obtained by aerosolizing the polymer

directly into the same aerosol mass spectrometer used during the field test. The match between the primary feature present in Figure 3a and Figure 3b is excellent. PDMS samples with different molecular weights (700, 1,500, and 2,500) are qualitatively similar, the only difference being that the ratio of m/z = 73 to the other peaks decreases with molecular weight.

238 Data from the engine test experiments identified the PDMS contaminant, but 239 could not verify the source of PDMS as the polymer is used in many common 240 applications and the contaminant has been observed in previous aerosol characterization 241 experiments. Hayden et al. (2008) reported a siloxane contaminant resulting from a silicone sealant used in a counter-flow virtual impactor. Since we did not use silicone 242 243 sealant in any particle accessible regions of the sampling line, we dismissed sealant as a 244 potential contamination source. Other contaminant sources include the fuel tank and fuel 245 line seals, fuel additive, exhaust gas probes, and sample transfer lines may have plausibly 246 introduced PDMS into the particles. We dismissed the fuel-related options as we deemed 247 it unlikely that PDMS would survive the combustion process. Several different exhaust 248 gas extraction probes were used throughout the experiment and they yielded similar 249 PDMS signatures and quantities, leaving the common sample transfer lines – and the 250 silicone tubing used in them - as the most likely source of the PDMS contaminant. 251 We performed three tests to identify unequivocally the silicone tubing as the 252 source of the PDMS contaminant and to demonstrate that the artifact is not limited to 253 engine exhaust studies.

In one experiment, the size-resolved composition of particles emitted from a diffusion flame of kerosene fuel was characterized using on-line aerosol mass



vacuum aerodynamic diameter (nm)

257 Figure 4. Particle size distribution of organic material and polydimethylsiloxane (PDMS) 258 coated on soot particles generated by combustion of kerosene in a diffusion flame: a) 259 total mass loading of organic particles obtained using either silicone (shown) or stainless 260 steel tubing, b) ratio of PDMS to total organic obtained for using either silicone or 261 stainless steel tubing. Data were collected for an hour by an aerosol mass spectrometer. 262 When the silicone tubing is used, the mass loading of PDMS is about 10% of the total 263 organic material in the 30-100 size range and roughly 2% in the 400-800 nm range. The 264 size distribution of PDMS and organic material indicates well-mixed particle population 265 for both soot sized particles (30-100 nm) and accumulation mode particles (400-800 nm). 266

267 spectrometry. The combustion-generated particles were passed through either a 30.5 cm

test section of as-received conductive silicone tubing (0.953 cm o.d., 0.635 cm i.d.) or

- stainless steel tubing (0.635 cm o.d., 0.476 cm i.d.). Figure 4a shows the particle size
- 270 distribution attributed to organic PM in the soot while Figure 4b shows the ratio of
- 271 PDMS to organic as a function of particle size. Substantial PDMS pick up is evident on

272	the 30-100 nm vacuum aerodynamic diameter soot particles (roughly 10% by mass), and
273	the PDMS is present as an internally mixed aerosol together with soot particles (Timko et
274	al., 2008; Onasch et al., 2008). The silicone tubing data in Figure 4b show that organic
275	aerosol particles present in the air in our laboratory and used to dilute the primary exhaust
276	sample (i.e., the size mode greater than about 500 nm) picked up about 1-3 wt % of the
277	PDMS contaminant. Figure 4b shows that PDMS pick up was negligible when stainless
278	steel tubing replaced the silicone tubing, confirming the silicone tubing as the source of
279	the contaminant.
280	In a second experiment, designed to study heterogeneous chemistry (Smith et al.,
281	2009), we obtained independent evidence supporting our PDMS assignment using a high
282	resolution (m/ Δ m ~ 3,000 at m/z 184) mass spectrometer coupled with a soft-ionization
283	technique (10.5 eV VUV radiation). In this experiment, organic aerosol particles
284	(squalane: $C_{30}H_{62}$) were generated in a nucleation oven and later sampled into the aerosol
285	mass spectrometer through a short (1 m) section of silicone tubing. During post-
286	processing, evidence of PDMS compounds was observed in the mass spectra; the

287 contamination was strongest after the silicone tubing was inadvertently exposed to

288 methanol. The high resolution, soft-ionization instrument permitted us to obtain mass

- 289 defect spectrometry data for high m/z (m/z > 500) PDMS ions. Figure 5 presents
- 290 characteristic high resolution mass spectra data for the large PDMS fragment ions. The



Figure 5. High resolution ($\Delta m/m \sim 3,000$) mass spectrum for the PDMS contaminant obtained after soft-ionization using VUV radiation. Adjacent peaks are separated by 74.02 \pm 0.03 mass units, which corresponds to SiO(CH₃)₂ (m/z 74.02). The inset compares the experimental spectrum to the predicted isotopic fragmentation pattern for (SiO(CH₃)₂)₈SiOCH₃⁺.

297

distinct m/z series containing 503, 577, 651, 725, 799, 873, and 947 is clearly evident in

the data. In slight contrast to the EI ionization data presented in Figure 3, the difference

300 between consecutive peaks resulting from soft ionization is always 74 mass units. In fact,

for the high resolution spectra the exact difference is 74.02 ± 0.03 mass units, matching

302 the weight of the $SiO(CH_3)_2^+$ fragment ion within instrumental mass calibration

303 precision. The soft ionization series follows the distinct m/z pattern of 59 + 74(n),

indicating the molecular ion carrier is either of the series $SiO(CH_3)(SiO(CH_3)_2)_n^+$ or

305 SiH(CH₃)₂(SiO(CH₃)₂)_n⁺. Based partially on the (SiO(CH₃)₂)_n⁺ molecular ion carrier

306 observed with EI ionization, we suspect that the soft ionization carrier is of the

307	$SiO(CH_3)(SiO(CH_3)_2)_n^+$ series. As further support of the $SiO(CH_3)$ m/z 59 assignment,
308	the strongest cluster of peaks occurs at m/z 651.11(6) which more closely matches the
309	mass of $(SiO(CH_3)_2)_8SiOCH_3^+$ m/z 651.14(5) than $(SiO(CH_3)_2)_8SiH(CH_3)_2^+$ m/z
310	651.18(2). The inset to Figure 5 shows a close-up of the m/z 651 mass spectra region
311	side-by-side with the calculated isotopic pattern for $(SiO(CH_3)_2)_8SiOCH_3^+$. The isotopic
312	match is excellent, confirming our assignment of the SiO(CH ₃) ₂ monomer to the
313	observed spectrum.
314	In a third experiment, FTIR spectroscopy provided complementary identification
315	of siloxane condensed on soot particles collected on filters. The soot was produced in a
316	diffusion flame of methane and air (Kirchstetter and Novakov, 2007) and was collected
317	with three PTFE membrane filters (Pall Life Sciences, 2.0 μ m pore size) in stainless steel
318	holders immediately downstream of two sections of conductive silicone tubing (for 1.27
319	cm hose barb) and one section of 1.27 cm stainless steel tubing, each 75 cm long.
320	Heating tape was applied to the upstream end of one of the pieces of silicone tubing. The
321	air temperature four centimeters into the upstream ends of the heated and unheated
322	silicone tubing lines (the point of maximum temperature) was 51 and 24 °C, respectively.
323	The sampling airflow rate through each line and duration were 12 SLPM and 80 min,
324	respectively.
325	The soot was removed from the filter and pelletized with KBr. FTIR spectra
326	recorded in the transmission mode (Magna Nicolet 760) are shown in Figure 6. Peaks
327	corresponding to siloxane functional groups were observed in the soot collected through
328	the silicone tubing, but were not evident in the soot collected through the stainless steel



330

Figure 6. FTIR spectra of soot passed through equal lengths of stainless steel and silicone conductive tubing at room temperature (unheated), and heated silicone conductive tubing. Peaks in the spectra of the soot collected via silicone tubing correspond to siloxane functional groups and are not evident in the spectra of soot collected via stainless steel tubing. The distance between each tick mark on the vertical axis is 0.01 absorbance units.

337

tubing. We assigned the following bands to siloxane functional groups: CH₃ bending

 (1259 cm^{-1}) , asymmetric Si-O-Si vibration (1020-1111 cm⁻¹), and Si-(CH₃)₂ rocking

340 vibrations (805 cm^{-1}) (Wachholz et al., 1995).

341 **3. Consequences of Contamination from Conductive Silicone Tubing.** The emission

- 342 of organic contaminants from silicone tubing can have undesirable consequences. We
- 343 have identified three circumstances when using this type of tubing can lead to erroneous
- 344 conclusions about the mass concentrations and physical behavior of aerosol particles.
- 345 Our analysis has not been exhaustive (i.e., our results cannot be used quantitatively to

346 assess the potential contamination in experimental circumstances not described here); 347 however, our results do illustrate significant artifacts when sampling carbonaceous 348 aerosol particles and, to a lesser degree, CO_2 concentration measurements through carbon 349 impregnated silicone tubing. Therefore, we recommend caution be exercised when 350 silicone tubing is used for particle characterization experiments. 351 Consequence 1: Addition of Particle Mass. Having positively identified the siloxane 352 contaminant in the engine exhaust particles discussed above, we set out to quantify its 353 concentration. The $SiO(CH_3)_2$ monomer unit in PDMS has a distinct mass spectrum from 354 other hydrocarbon-like organic material (e.g. partially oxidized fuel in aircraft engine 355 exhaust and lubricating oils), which provides an opportunity to quantify the fraction of 356 particle material which is PDMS. Overlap between PDMS and hydrocarbon organic 357 compounds occurs at m/z 55, 57, etc; these peaks constitute less than 5% of the total 358 PDMS spectrum and were assumed to be entirely organic. Based on the limited overlap 359 between PDMS and other interfering species, we estimate our PDMS detection limit to be 50 ng m⁻³ in the presence of engine exhaust (for a 10 sec sampling period). In the 360 361 absence of any interference, our detection limit, calculated as three times the measurement noise, is 3 ng m⁻³ (for a 10 sec sampling period). The characteristic PDMS 362 363 peak at m/z 73 was distributed between PDMS and organic assuming that the organic 364 contribution at m/z 73 was the average value of m/z 87 and m/z 59 (corresponding to 365 addition and subtraction of a - CH_2 group, respectively), according to a common mass 366 spectrometry analysis procedure (Allan et al., 2004). The other major characteristic 367 PDMS peaks at m/z = 147, 207, 221, etc. were assumed to be entirely due to PDMS. 368 With these assumptions, we calculate that PDMS constitutes about 30% of the entire

369	particle mass defined as "organic" in the spectrum pictured in Figure 3a. Similarly,
370	roughly 10% of the organic mass present on the laboratory soot (Figure 4) was PDMS.
371	Instruments designed to measure total particle mass loadings would have overestimated
372	semi-volatile organic PM (that is, particle mass which exists in the gas phase at
373	temperatures greater than 100 $^{\circ}$ C) by up to 30% for these two specific cases, and without
374	corresponding chemical composition information the data could not have been corrected
375	during post-processing.
376	Consequence 2: Positive mass bias in filter-based techniques. On-line aerosol mass
377	spectrometry is a powerful technique, but it is not as commonly practiced as filter
378	collection of particle samples and off-line analysis. We performed simple tests which
379	indicate that silicone tubing may introduce a positive mass bias for filter-based
380	techniques used to measure concentrations of carbonaceous particulate matter. In these
381	tests, quartz fiber filters (Pallflex 2500 QAT-UP) were used to sample air that had passed
382	through parallel sections of tubing: heated silicone, unheated silicone, and unheated
383	stainless steel (the same as used in the experiments that produced Figure 6). The
384	sampling flow rate and duration were 10 SLPM for 55 min in each case. The air was
385	initially particle free and scrubbed of organic gases using an activated carbon denuder.
386	The air temperature at four centimeters into the upstream ends of the heated and unheated
387	silicone tubing lines in this experiment was 45 and 22 °C, respectively.
388	The carbon content of each filter was quantified using the thermal analysis
389	technique of Kirchstetter and Novakov (2007). The carbon evolved from each filter as it
390	was heated is shown in Figure 7a. The filters downstream of both the heated and
391	unheated silicone tubing collected significant amounts of carbon; the former collected

392 about 50% more mass than the latter. In contrast, the filter downstream of the stainless 393 steel tubing was comparatively free of carbon, proving that carbon on filters downstream 394 of the silicone tubing was emitted by the silicone tubing. The features of the carbon 395 thermograms – both the relative heights and temperatures of the primary peak and 396 secondary peaks are consistent with those of sorbed organic vapors on quartz filters 397 (Kirchstetter et al., 2001). Figure 7b shows thermograms of two quartz filters 398 downstream of the same section of heated silicone tubing in similar experiment in which 399 one quartz filter was preceded by a PTFE membrane filter. The particle removal 400 efficiency of the PTFE membrane is essentially 100%, so the presence of carbon on the 401 backup quartz filter proves that this carbonaceous material was gaseous rather than 402 particulate when it was collected, demonstrating that particles are not required to carry 403 the vapors emitted from the silicone tubing. We infer that the vapor is likely the siloxane 404 compound identified above. Our observations are consistent with the diffusion of low 405 molecular weight siloxanes from the bulk to the surface of the silicone tubing wall as 406 described by Hunt et al (2002) and Oláh et al. (2005), followed by their release into the 407 vapor phase. 408 While the collection of particulate matter with quartz fiber filters and the

409 subsequent thermal analysis of the filters is a widely used method for quantifying 410 concentrations of carbonaceous particulate matter, the technique is prone to a major 411 sampling artifact: the adsorption of organic vapors to the quartz filters. The adsorbed 412 vapors on the filter, in addition to the collected particulate matter, evolve during thermal 413 analysis. Particulate carbon concentrations derived from this analysis will, therefore, be





416

417

418 Figure 7. Evolution of carbon as a function of temperature for (a) quartz filters that were 419 used to sample particle free air through heated and unheated silicone conductive tubing 420 and unheated stainless steel tubing and (b) a front and a backup quartz filter collected 421 downstream of heated silicone conductive tubing.

- 422
- 423

424 overestimated if the adsorbed carbon is not discounted. This artifact is known as the425 positive sampling artifact for particulate carbon.

426 The experiments described above illustrated that the use of silicone conductive 427 tubing results in the adsorption of organic vapors to quartz filters. If this carbon is 428 mistaken as particulate, the apparent particulate carbon concentrations for the "heated" 429 and "unheated" quartz filter samples collected through silicone tubing shown in Figure 7a are 64 and 39 μ gC m⁻³ for the experimental configuration and tubing lengths used here. 430 431 (The concentrations of contaminant vapor present in the sampled air stream were most 432 likely larger than these estimates because quartz filters generally remove only a fraction 433 of the vapor to which they are exposed.) While heating the tubing enhanced the artifact, 434 the positive bias still large (compared to typical atmospheric carbon particulate matter 435 concentrations, for example) in the case when the tubing was not heated.

436 A sampling method recommended to quantify the magnitude of the positive 437 artifact – and to correct for it – involves sampling with a backup quartz filter, either 438 placed behind the primary quartz filter or behind a PTFE membrane filter (Turpin et al., 439 1994). This method works well if the backup and front quartz filters adsorb comparable 440 amounts of organic vapors, in which case the amount of carbon on the back quartz filter 441 can be subtracted from the amount of carbon on the front quartz filter. As shown for the 442 experiment depicted in Figure 7b, the quartz filter behind the PTFE membrane filter 443 provided a good measure of the artifact. In most published instances, however, this 444 correction is not applied to particulate carbon concentrations (Novakov et al., 2005). 445 Consequence 3: Alteration of Particle Surface Properties. In addition to the quantitative 446 biases observed for aerosol mass spectrometry and filter collection and analysis, we

447 observed that the silicone tubing can alter the surface of sampled particles. Specifically 448 during the production of suspensions of soot in water for various research applications, 449 we observed that passing of soot through silicone conductive tubing altered its water 450 affinity. Our production of soot suspensions involved 1) collecting soot generated with a 451 diffusion flame of methane and air through stainless steel tubing onto a stretched PTFE 452 membrane filter, 2) exposing the soot-laden filter to ozone via PTFE tubing, and 3) 453 rinsing the soot from the filter with water and collecting it in a beaker. At that point, a 454 simple swishing of the water formed a stable soot suspension (Figure 8a). The ozonation 455 step leads to the formation of polar surface groups, such as carboxylates (Smith and 456 Chughtai, 1997), which apparently transforms the soot from a hydrophobic to a 457 hydrophilic state. If the ozonation step was skipped, the soot remained hydrophobic and 458 would not wet, clustering at the water surface.

459



461 **Figure 8.** (a) Soot from a diffusion flame made hydrophilic by reaction with ozone.

462 Shown is the soot as it is mixing with water. (b) Soot from a diffusion flame that does not

463 mix with water despite ozone exposure. The soot in (b) was collected through silicone

464 conductive tubing as opposed to the soot in (a), which was collected through stainless

465 steel tubing.

466	The influence of the silicone tubing was noted when the first step of our method
467	was altered to include a 75 cm length of silicone conductive tubing in lieu of stainless
468	steel tubing. In this case, the soot particles did not evenly disperse in the water. The
469	effect was markedly enhanced when the inlet to the silicone tubing was heated to 45 $^{\circ}$ C.
470	For heated silicone tubing, the soot remained hydrophobic and was completely non-
471	wettable, as shown in Figure 8b.
472 473	We considered the mechanism preventing the soot's transformation to a
474	hydrophilic state, though it remains an open question. Adsorbed siloxanes may inhibit
475	(i.e., poison) the surface oxidation reaction necessary for making the soot hydrophilic.
476	FTIR measurements, however, indicated the formation of hydrophilic (Chughtai et al.,
477	1991) carboxyl groups upon ozonation in samples of soot regardless of whether they had
478	passed through the heated silicone or unheated stainless steel tubing. Another possibility
479	is that the adsorbed vapor was hydrophobic and rendered the soot hydrophobic despite its
480	surface oxidation. We observed in the experiments described above that the adsorption
481	of the vapor emitted by the silicone tubing onto quartz filters increased their
482	hydrophobicity, supporting this hypothesis. A drop of water placed on the "heated
483	silicone tubing" filter (referenced in Figure 7a) remained on its surface whereas a water
484	drop placed on the "unheated stainless steel tubing" filter was immediately soaked into
485	the filter, demonstrating the hydrophobic nature of the vapor emitted by the silicone
486	tubing. FTIR measurements indicated the continued presence of the siloxane during
487	ozonation, and while these data do not give a complete description of the soot surface,
488	they suggest that the persistence of the siloxanes may render the soot hydrophobic even
489	though some oxidation of the soot may occur.

490	4. Mechanisms of Siloxane Uptake by Particles. Experimental observations suggest
491	that the PDMS entrainment mechanism primarily involves gas-to-particle transfer of
492	short-chain PDMS oligomers. Transfer of PDMS polymers into the sample stream via
493	direct entrainment of loose particles (i.e., particle entrainment) is another plausible
494	mechanism. Freshly received silicone tubing sporadically generated PDMS particles (1
495	particle event every 30-60 sec) when filtered air was passed through it at room
496	temperature (>50 ng m ⁻³). However, gas-to-particle uptake was much more significant
497	than the small contribution due to particle entrainment. As suggested in Figure 4, PDMS
498	was typically present as an internally mixed aerosol, together with an organic fraction.
499	PDMS particles shed directly from the tubing wall would likely be present as an
500	externally mixed aerosol population. Only the gas-to-particle mechanism would lead to
501	the internally mixed aerosol populations observed experimentally.
502	The quartz filter experiments discussed above provide the best evidence that gas-
503	to-particle transfer must occur. In these experiments, a quartz filter placed downstream
504	of a PTFE membrane collected organic carbon while sampling purified air that had
505	contacted the silicone tubing. The collection of carbon could only have occurred due to
506	adsorption of gaseous materials – i.e., siloxane – that had evaporated from the silicone
507	tubing. In the presence of a particle carrier, the siloxane materials would also condense
508	on the particles. Therefore, we conclude that gas-to-particle conversion must be an
509	important mechanism whereby siloxane is introduced to the particles.
510	Gentle heating (<70 $^{\circ}$ C), particle carriers, and exposure to organic solvents
511	enhance siloxane uptake. Table 1 summarizes our observations of PDMS uptake
512	alongside experimental conditions. Transporting the soot particles through room

temperature silicone tubing reduced the effectiveness of an ozone treatment to make the soot hydrophilic. Heating the silicone tubing completely negated the effectiveness of the ozonation treatment. PDMS uptake onto squalane particles did not occur until the silicone tubing was inadvertently exposed to methanol. PDMS uptake onto soot was more pronounced at slightly elevated temperatures (< 70 °C, estimated based on energy balance considerations) than at room temperature, even though the exposure time was an order of magnitude shorter.

520 In addition to solvent exposure and temperature, particle composition and surface 521 area may also be important. We have tested PDMS uptake behavior for a range of 522 particles: soot particles (generated in a high pressure gas turbine engine and in an 523 atmospheric pressure diffusion flame burners, 50 nm $< D_{VA} < 120$ nm), lubrication oil droplets (generated by a gas turbine engine or atomization, $100 \text{ nm} < D_{VA} < 400 \text{ nm}$), 524 525 organic aerosol (squalane generated from atomizing a methanol solution) and ambient 526 particles (present in both outdoor and laboratory air), and ambient sulfate particles 527 present at Jupiter, FL ($D_{VA} > 100 \text{ nm}$). PDMS uptake ranged from below detection limits $(50 \text{ ng m}^{-3} \text{ in the presence of organic interference such as from engine exhaust, 3 ng m}^{-3}$ 528 in filtered air) to 1000 ng m⁻³. Depending on the exact source and sampling 529 530 configuration, uptake onto soot particles accounted for 20-30% of the total organic particle mass (absolute quantity ≈ 200 to 1000 ng m⁻³). Lubrication oil droplets picked 531 532 up much less PDMS than soot – on the order of 1-2% by weight or absolute quantities of 533 about 10-50 ng m⁻³. Insufficient PDMS was present on the lube oil to confirm coincident 534 size distributions. PDMS content in poorly characterized organic particles present in 535 laboratory air was about 5% by mass (as shown in Figure 4). PDMS pickup by ambient

sulfate particles was below the instrument detection limits as PDMS constituted less than 0.1% of the sulfate particle mass (corresponding to a gas concentration of between 3-10 $m m^{-3}$).

539 In their studies of diesel combustion exhaust from a camp stove burner, Schneider 540 et al. (2006) found that particles produced in fuel rich flames (with a modal aerodynamic 541 diameter of 60 nm) picked up the PDMS contaminant from the silicone tubing, while 542 particles produced in oxygen rich flame (with modal aerodynamic diameters ranging 543 from 120-180 nm) did not. Since the fuel rich flames produced soot particles whereas the 544 oxygen rich flames did not, the authors infer that the PDMS contaminant partitions 545 preferentially onto soot. Schneider et al. (2006) also report PDMS contamination of soot 546 particles produced by a spark soot generator.

547 Yu et al. (2009) report siloxane uptake onto NaNO₃ particles (83 nm geometric mean diameter). The quartz filters picked up 4 ng m^{-3} of siloxane when dry air was 548 passed through a 0.30 m section of silicone tubing and 14.9 ng m⁻³ for a 3.3 m tubing 549 550 length. After passing through 3.3 m of silicone tubing, salt particles deposited 22.9 ng m⁻³ of siloxane material on the quartz filter (RH = 10%). The quantity of PDMS 551 552 decreased with increasing relative humidity for both particle free air and salt particles, 553 though the authors note that increasing humidity may increase PDMS partitioning to the 554 particle phase in some instances.

555

556 5. Conclusions and Recommendations. Conductive silicone tubing use is associated
557 with two sampling artifacts: 1) erroneous CO₂ concentration measurements due to
558 dynamic uptake of CO₂ and 2) contamination by polydimethylsiloxane (PDMS) vapors.

559	Contamination by PDMS inflates particle mass measurements made by aerosol mass
560	spectrometry and filter deposition methods. Moreover, PDMS pickup may alter particle
561	surface properties, specifically the hydrophobic/hydrophilic balance. We recommend
562	further tests be performed to evaluate the influence of silicone tubing on the water-uptake
563	of soot in in-situ aerosol hygroscopic growth experiments. Contamination associated
564	with the use of silicone tubing was observed at room temperature and, in some cases, was
565	enhanced by mild heating (>70 $^{\circ}$ C). The experimental evidences warrants further
566	evaluation of the effects of temperature, physicochemical properties of the particle
567	carriers, sample contact time, and tubing age on particle contamination by silicone
568	tubing. Despite its convenient flexibility and charge dissipation properties, we
569	recommend that conductive silicone tubing be used with care for aerosol test
570	experiments.
571	In some instances, the advantages of silicone tubing may outweigh its
572	disadvantages. In these cases, we recommend that special precautions be made to
573	manage potential errors. Specifically, when sampling particulate matter onto a quartz
574	filter through silicone tubing to quantify particulate carbon concentration by thermal
575	analysis, we recommend the simultaneous use of a backup quartz filter to correct for the
576	adsorption of organic vapors to the quartz filter.
577	
578	Acknowledgments. The Aerodyne Research Inc. team thanks NASA (NRA
579	#NNC07CB57C) for supporting this work. We thank Bruce Anderson (NASA, Langley

580 Research Center) for his continued support of gas turbine engine particle emissions

581 characterization and useful discussion during the drafting of this manuscript. Brent

582 Williams (Aerodyne Research, Inc. and University of Minnesota) shared results from his

- 583 GC/MS analysis of siloxanes. Kathleen Tacina, Dan Bulzan, and Nan-Suey Liu (NASA
- 584 Glenn Research Center); Andreas Beyersdorf (NASA Langley Research Center); and
- 585 Anuj Bhargava (Pratt & Whitney) provided helpful discussion and comments which
- 586 improved the manuscript. Measurements at the Chemical Dynamics Beamline at the
- 587 Advanced Light Source are supported by the Director, Office of Energy Research, Office
- 588 of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy
- under Contract No. DE AC02-05CH11231. J.D.S is also supported by the Camille and
- 590 Henry Dreyfus foundation postdoctoral program in environmental chemistry.
- 591
- 592

593 **References.**

Allan, J. D., A. E. Delia, H. Coe, K. N. Bower, M. R. Alfarra, J. L. Jimenez, A. M.
Middlebrook, F. Drewnick, T. B. Onasch, M. R. Canagaratna, J. T. Jayne and D. R.
Worsnop, (2004) A Generalised Method for the Extraction of Chemically Resolved Mass
Spectra from Aerodyne Aerosol Mass Spectrometer Data. *Journal of Aerosol Sci.*35(7):909-922.

Brockman, J. E. (1993). Sampling and Transport of Aerosols, in Aerosol Measurement:
Principles, Techniques, and Applications, K. Willeke and P. A. Baron, ed., John Wiley &
Sons, Inc., New York, pp 77-108.

- Canagaratna, M. R., Jayne, J. T., Jimenez, J. L., Allan, J. D., Alfarra, M. R., Zhang, Q.,
 Onasch, T. B., Drewnick, F., Coe, H., Middlebrook, A., Delia, A., Williams, L. R.,
 Trimborn, A. M., Northway, M. J., DeCarlo, P. F., Kolb, C. E., Davidovits P., and
 Worsnop, D. R. (2007). Chemical and Microphysical Characterization of Ambient
 Aerosols with the Aerodyne Aerosol Mass Spectrometer. *Mass Spec. Rev.* 26:185-222.
- 607 Chughtai, A. R., Jassim, J. A., Peterson, J. H., Stedman, D. H., Smith, D. M. (1991)
- 608 Spectroscopic and Solubility Characteristics of Oxidized Soots. *Aerosol Sci. Tech.*609 15:112-126.
- 610 Dong, X., Gusev, A., and Hercules, D.M. (1998). Characterization of Polysiloxanes with
- 611 Different Functional Groups by Time-of-Flight Secondary Ion Mass Spectrometry. J. 612 American Soc. Mass Spec. 9:292:298.

- Hayden, K. L., Macdonald, A. M., Gong, W., Toom-Sauntry, D., Anlauf, K. G., Leithead,
- A., Li, S.-M., Leaitch, W. R., Noone, K. (2008) Cloud Processing of Nitrate. J. Geophys.
- 615 Res. 113, doi:10.1029/2007/JD009732.
- Hinds, W. C. Aerosol Technology: Properties, (1999). Behavior, and Measurement of
 Airborne Particles. 2nd ed. John Wiley & Sons, Inc., New York, pp. 206-232.
- Hunt, S., Cash, G., Liu, H., George, G., Birtwistle, D. (2002) Spectroscopic
- 619 Characterization of Low Molecular Weight Fluids from Silicone Elastomers. J.
- 620 *Macromolecular Science A* A39:1007-1024.
- 621 Jayne, J. T., Leard, D. C., Zhang, X. F., Davidovits, P., Smith, K. A., Kolb, C. E., and
- 622 Worsnop, D. R. (2000). Development of an Aerosol Mass Spectrometer for Size and
- 623 Composition Analysis of Submicron Particles. *Aerosol Sci. Technol.* 33:49-70.
- 624 Kirchstetter, T. W., Corrigan, C. E., Novakov, T. (2001) Laboratory and Field
- 625 Investigation of the Adsorption of Gaseous Organic Compounds onto Quartz Filters.
- 626 *Atmos. Environ.* 35:1663-1671.
- 627 Kirchstetter, T.W. Novakov, T. (2007) Controlled Generation of Black Carbon Particles
- 628 from a Diffusion Flame and Applications in Evaluating Black Carbon Measurement
- 629 Methods. *Atmos. Environ.* 41:1874-1888, doi:10.1016/j.atmosenv.2006.10.067.
- 630 Kumar, P., Fennell, P., Symonds, J., Britter, R. Treatment of Losses of Ultrafine Aerosol
- Particles in Long Sampling Tubes during Ambient Measurements. *Atmos. Environ.*42:8819-8826.
- Lobo, P., Hagan, D. E., Whitefield, P. D., Alofs, D. J. (2007). Physical Characterization
 of Aerosol Emissions from a Commercial Gas Turbine Engine. *J. Power Prop.* 23:919929.
- 636 Novakov T., Menon S., Kirchstetter T. W., Koch, D. Hansen, J. E. (2005) Aerosol
- 637 Organic Carbon to Black Carbon Ratios: Analysis of Published Data and Implications for 638 Climate Forcing, *J. Geophys. Res.* 110:D21205.
- 639 Oláh, A., Hillborg, H., Vancso, G. J. (2005) Hydrophobic Recovery of UV/ozone Treated
- 640 Poly(dimethylsiloxane): Adhesion Studies by Contact Mechanics and Mechanism of
- 641 Surface Modification. *Appl. Surf. Sci.* 239:410-423.
- Onasch, T. B., Jayne, J. T., Herndon, S. C., Mortimer, I. P., Worsnop, D. R., Miake-Lye,
 R. C., Chemical Properties of Aircraft Engine Particulate Exhaust Emissions Sampled
 during APEX. *J. Power Prop.* accepted.
- 645 Schneider, J., Weimer, S., Drewnick, F., Borrman, S. Helas, G., Gwaze, P., Schmid, O.,
- 646 Andreae, M. O., Kirchner, U. (2006). Mass Spectrometric Analysis and Aerodynamic
- 647 Properties of Various Types of Combustion-Related Aerosol Particles. Int. J. Mass Spec.
- 648 258:37-49.

- 649 Smith, D. M., Chughtai, A. R. (1997) Photochemical Effects in the Heterogeneous
- 650 Reaction of Soot with Ozone at Low Concentrations. J. Atmos. Chem, 26:77-91.
- 651 Smith, J. D., Kroll, J. H., Cappa, C. D., Che, D. L., Liu, C. L., Ahmed, M., Leone, S. R.,
- Worsnop, D. R., Wilson, K. R. (2009) The Heterogeneous Reaction of Hydroxyl Radicals
- 653 with Sub-micron Squalane Particles: A Model System for Understanding the Oxidative
- 654 Aging of Ambient Aerosols. Atmos. Chem. Phys. submitted.
- Timko, M. T., Onasch, T. B., Northway, M. J., Jayne, J. T., Canagaratna, M., Herndon, S.
- 656 C., Wood, E. C., Miake-Lye, R. C. (2009) Gas Turbine Engine Emissions Part 2.
- 657 Chemical Properties of Particulate Matter. *manuscript in preparation*.
- Timko, M. T., Beyersdorf, A. J., Bhargava, A., Winstead, E. L., Thornhill, K. L.,
 Liscinsky, D. S., Souza, J., Wey, C., Tacina, K., Yu, Z., Onasch, T. B., Miake-Lye, R. C.,
 Corporan, E., DeWitt, M. J., Klingshirn, C., Howard, R., Anderson, B. E. (2009) Effects
 of a Fischer-Tropsch Syntetic Fuel on the Emissions Performance of a Gas Turbine
 Engine. *manuscript in preparation*.
- Turpin, B. J., Huntzicker, J. J., Hering, S. V. (1994) Investigation of the Organic Aerosol
 Sampling Artifacts in the Los Angeles Basin. *Atmospheric Environment* 28:3061-3071.
- 665 Wachholz, S., Keidel, F., Just, U., Geissler, H., Kappler, K. (1995) Analysis of a Mixture
- of Linear and Cyclic Siloxanes by Cryo-Gas Chromatography-Fourier Transform
- Infrared Spectroscopy and Gas Chromatography-Mass Spectrometry. *J Chromat. A.*668 693:89-99.
- 669 Wey, C. C., Anderson, B. E., Hudgins, C., Wey, C., Li-Jones, X., Winstead, E.,
- 670 Thornhill, L. K., Lobo, P., Hagen, D., Whitefield, P., Yelvington, P. E., Herndon, S. C.,
- 671 Onasch, T. B., Miake-Lye, R. C., Wormhoudt, J., Knighton, W. B., Howard, R., Bryant,
- D., Corporan, E., Moses, C., Holve, D., Dodds, W. (2006) Aircraft Particle Emissions
- 673 eXperiment (APEX). NASA/TM-2006-214382.
- 674 Yu, Y., Alexander, M. L., Perraud, V., Bruns, E. A., Johnson, S. N., Ezell, M. J.,
- 675 Finlayson-Pitts, B. J. Contamination from Electrically Conductive Silicone Tubing during
- 676 Aerosol Chemical Analysis. *Atmos. Environ.* doi:10.1016/j.atmosenv.2009.02.014.

677 Figure Captions

678 **Figure 1.** Fractional penetration (transmission) of size selected soot particles through test

679 sections of stainless steel, conductive silicone, and polyvinyl chloride tubing. Fractional 680 penetration is nearly identical for stainless steel, and conductive silicone tubing.

681 Electrostatic losses in the non-conducting polyvinyl chloride tubing greatly reduce

682 particle transmission. The penetration calculated for conductive tubing is shown for

- reference. Calculated penetration includes losses due to diffusion and inertia (settling),
- but not electrostatic losses. Conditions: 50 SLPM flow rate, 1.27 cm i.d. tubing, 50m
- tubing length, 25°C, 1 bar pressure.

Figure 2. CO_2 concentrations in air dilution gas (initially 50,000 ppm CO_2) directly from the flow manifold and after transport through 15.2 m of stainless steel or 15.2 m of conductive silicone tubing. The CO_2 concentration is about 5% lower after transport through silicone tubing as compared to its concentration direct from the manifold or after transport through stainless steel tubing. The CO_2 concentration after transmission through silicone tubing appears to slowly recover, but the dynamic response time is

692 greater than 5 min.

693 **Figure 3.** Characteristic EI ionization mass spectra obtained for a) engine exhaust

694 particles and b) aerosolized polydimethylsiloxane (PDMS). The m/z features distinctive 695 of PDMS, (m/z = 73, 147, 207, 221, 281) are readily apparent as a contaminant in the 696 engine exhaust particles.

Figure 4. Particle size distribution of organic material and PDMS coated on soot particlesgenerated by combustion of kerosene in a diffusion flame. Data were collected over the

699 course of an hour by an aerosol mass spectrometer. The mass loading of PDMS is about

- 10% of the total organic material in the 30-100 size range. The size distribution of
- 701 PDMS and organic material indicates well-mixed particle population for soot sized
- 702 particles (30-100 nm). Ambient organic aerosol present in the laboratory during the
- testing period (diameter > 200 nm) has measurable but lower capacity for PDMS
- compared to the soot particles. The ratio of the organic scale to the PDMS scale is 12:1.
- Figure 5. High resolution ($\Delta m/m \sim 3,000$) mass spectrum for the PDMS contaminant
- 706 obtained after soft-ionization using VUV radiation. Adjacent peaks are separated by
- 707 74.02 ± 0.03 mass units, which corresponds to SiO(CH₃)₂ (m/z 74.02). The inset
- compares the experimental spectrum to the predicted isotopic fragmentation pattern for $(SiO(CH_3)_2)_8SiOCH_3^+$.
- 710 **Figure 6.** FTIR spectra of soot passed through equal lengths of stainless steel and

silicone conductive tubing at room temperature (unheated), and heated silicone

712 conductive tubing. Peaks in the spectra of the soot collected via silicone tubing

- correspond to siloxane functional groups and are not evident in the spectra of soot
- collected via stainless steel tubing. The distance between each tick mark on the vertical
- 715 axis is 0.01 absorbance units.
- 716 **Figure 7.** Evolution of carbon as a function of temperature for (a) quartz filters that were
- 717 used to sample particle free air through heated and unheated silicone conductive tubing
- and unheated stainless steel tubing and (b) a front and a backup quartz filter collected
- 719 downstream of heated silicone conductive tubing.

- 720 **Figure 8.** (a) Soot from a diffusion flame made hydrophilic by reaction with ozone.
- 721 Shown is the soot as it is mixing with water. (b) Soot from a diffusion flame that does not
- mix with water despite ozone exposure. The soot in (b) was collected through silicone
- conductive tubing as opposed to the soot in (a), which was collected through stainless
- steel tubing.