Supplemental Information : Secondary Organic Aerosol Production from Modern Diesel Engine Emissions, Shar Samy and Barbara Zielinska

Table S1. Composition of VOC mixtures

Compound	**Density g/ml**	**Mixture #1**	**Added to chamber 10 µl**	**Concentrations in chamber (µg/m³)**	**Mixture #2**	**Added to chamber 100 µl**	**Concentrations in chamber (µg/m³)**
Benzene	0.88	None	None	None	75 µl	5.94 µl	26
o-Xylene	0.87	None	None	None	175 µl	13.86 µl	60
p-Cymene	0.86	50 µl	2.63 µl	11	250 µl	19.80 µl	85
1,2 - Diethylbenzene	0.86	50µl	2.63 µl	11	250 µl	19.80 µl	85
1,2,4-Trimethylbenzene	0.88	40 µl	2.11 µl	9.0	200 µl	15.84 µl	70
iso-Butylbenzene	0.85	50 µl	2.63 µl	11	250 µl	19.80 µl	84
Naphthalene	solid	1.9 mg	1.9 mg	9.5	37.3 mg	2.95 mg	15
1,2,4,5-Tetramethylbenzene	solid	1.6 mg	1.6 mg	8.0	25.2 mg	2.0 mg	10

Mixture #1 was added only to exposure D-2 (06/01/06; DE+ NO_3+VOC). Mixture #2 was added to exposures L-1b (06/02/06; DE+sun+VOC) and L-2b (06/07/06; DE+sun+OH+VOC)

Table S2. List of POC analyzed in this study

Alkanoic acids	***Alkanedioic acids***	***Aromatic acids***
Full Compound Name	**Full Compound Name**	**Full Compound Name**
hexanoic acid (c6*)	oxalic acid (d-c2)	phenylacetic acid
heptanoic acid (c7)	malonic acid (d-c3)	o-toluic
octanoic acid (c8)	me-malonic (d-c3)	m-toluic
nonanoic acid (c9)	maleic acid (d-c4)	p-toluic
decanoic acid (c10)	succinic acid (d-c4)	2,6-dimethylbenzoic acid
undecanoic acid (c11)	me-succinic acid (d-c5)	2,5-dimethylbenzoic acid
myristoleic acid (c14)	glutaric acid (d-c5)	2,4-dimethylbenzoic acid
myristic acid (c14)	2-methylglutaric (d-c6)	3,5-dimethylbenzoic acid
pentadecanoic acid (c15)	3-methylglutaric acid (d-c6)	3,4-dimethylbenzoic acid
palmitic acid (c16)	hexanedioic (adipic) acid (d-c6)	2,3-dimethoxybenzoic acid
isostearic acid (c18)	3-methyladipic acid (d-c7)	2,6-dimethoxybenzoic acid
oleic acid (c18)	heptanedioic (pimelic) acid (d-c7)	2,5-dimethoxybenzoic acid
elaidic acid (c18)	suberic acid (d-c8)	phthalic acid
stearic acid (c18)	azelaic acid (d-c9)	isophthalic acid
nonadecanoic acid (c19)	sebacic acid (d-c10)	
eicosanoic acid (c20)	undecanedioic acid (d-c11)	
heneicosanoic acid (c21)	dodecanedioic acid (d-c12)	
docosanoic acid (c22)	traumatic acid (d-c12)	
tricosanoic acid (c23)	1,11-undecanedicarboxylic acid (d-c13)	
tetracosanoic acid (c24)	1,12-dodecanedicarboxylic acid (d-c14)	

*c# = carbon number, d = di-acid

Distinct POC production in light versus dark experiments suggests the role of OH initiated reactions in these chamber atmospheres (Finlayson-Pitts and Pitts, 2000). Many of these compounds are thought to be formed by photooxidation reactions of VOC and SVOC, which result in SOA formation (Kleindienst et al., 2002; 2004).

The significant difference between the 2005 and 2006 L-3 experiments (Table S3) may be due to several factors, including: engine age or total engine lifetime operation, differences in the initial in-chamber toluene mixing ratios (639 +/- 32 for 2005; 524 +/- 6 for 2006), total DE aging time of the individual experiments (~5 hrs. for 2005; ~4 hrs. for 2006), and difference in the initial DPM mass concentrations (10.1 +/- 1.4 $\mu g/m^{-3}$ for 2005; 36.8 +/- 5.5 $\mu g/m^{-3}$). In addition, as the engine becomes older changes in the engine components (e.g. valves, seals, internal surfaces) may result in corollary changes in the emissions. For more detail on compositional and toxicity changes produced from further diesel engine use, see Zielinska et al. (2009).

Table S3. 2005 SOA % production values, pre-sampling mass has been corrected for wall-loss.

Date	Experiment	Post-injection Time (GMT)	Post-injection mass (μgm^{-3})	Pre-Sampling Time (GMT)	Pre-sampling mass (μgm^{-3})	Mass Difference (μgm^{-3})	%SOA of Final Mass
05/16/05	D-3, Diesel in Dark with ozone	9:15	11.5	15:30	11	-0.5	0.0
05/17/05	D-3, Diesel in Dark with ozone	10:18	12.9	15:18	12.8	-0.1	0.0
05/12/05	L-1, Diesel in Light	10:23	11.7	15:18	11.8	0.1	0.8
05/11/05	L-1, Diesel in Light	10:31	9.8	15:16	10.4	0.6	5.8
05/13/05	L-2, Diesel in Light with HCHO	9:17	8.2	15:32	9.8	1.6	16.3
05/18/05	L-2, Diesel in Light with HCHO	9:13	13.8	15:38	16.6	2.8	16.9
05/19/05	L-3, Diesel in Light with toluene	8:15	9.1	13:35	70.5	61.4	87.1
05/20/05	L-3, Diesel in Light with toluene	8:57	11.1	13:52	75.2	64.1	85.2

Table S4. Gas phase concentrations (μg mg^{-1}EC) for POC.

Alkanoic acids (gas phase)	**L-1a**	**L-1b (VOC)**	**L-2a**	**L-2b (VOC)**	**L-3a (TOL)**	**L-3b (TOL)**	**D-1**	**D-2 (VOC)**
hexanoic acid	16.1	39.7	126.5	0.0	330.4	13.4	137.9	141.9
heptanoic acid	45.5	146.0	138.7	351.6	961.5	171.9	106.6	184.5
octanoic acid	20.7	129.9	102.7	79.0	265.8	18.8	135.8	249.7
nonanoic acid	25.7	245.6	179.7	116.6	445.3	38.0	213.2	458.0
decanoic acid	20.9	261.3	99.7	80.0	306.6	21.1	188.7	548.5
undecanoic acid	0.0	0.0	0.0	0.0	65.4	5.4	34.5	55.5
myristoleic acid	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
myristic acid	2.1	27.8	28.9	4.7	48.1	3.5	63.2	33.7
pentadecanoic acid	1.1	11.5	11.9	3.6	22.5	1.5	18.8	15.9
palmitic acid	0.0	85.5	135.1	0.0	223.8	9.6	173.9	132.8
isostearic acid	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
traumatic acid	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
oleic acid	0.0	24.8	15.2	0.0	14.5	1.8	52.6	73.2
elaidic acid	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
stearic acid	0.0	57.4	72.5	0.0	125.4	5.3	103.7	71.6
nonadecanoic acid	0.0	20.2	26.7	0.0	26.9	7.8	20.0	0.0
eicosanoic acid	0.0	0.0	0.0	0.0	10.0	0.0	8.9	0.0
heneicosanoic acid	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
docosanoic acid	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
tetracosanoic acid	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
sum	*132*	*1050*	*938*	*635*	*2846*	*298*	*1258*	*1965*

Alkanedioic acids (gas phase)	**L-1a**	**L-1b (VOC)**	**L-2a**	**L-2b (VOC)**	**L-3a (TOL)**	**L-3b (TOL)**	**D-1**	**D-2 (VOC)**
oxalic acid	57.9	0.0	135.6	692.9	649.2	132.0	194.6	0.0
malonic acid	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
me-malonic	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
maleic acid	8.8	0.0	0.0	0.0	558.8	69.0	72.9	35.3
succinic acid	92.5	99.4	512.4	279.2	625.5	48.3	138.6	155.7
me-succinic acid	8.3	23.8	57.2	39.6	133.0	24.0	29.6	35.9
glutaric acid	27.7	0.0	94.9	70.2	256.1	12.8	35.2	0.0
2-methylglutaric	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
3-methylglutaric acid	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
hexanedioic (adipic) acid	6.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0
3-methyladipic acid	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
heptanedioic (pimelic) acid	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
suberic acid	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
azelaic acid	0.0	3.5	46.8	0.0	46.9	0.1	271.4	0.0
sebacic acid	0.0	0.0	0.0	0.2	3.8	0.0	2.1	0.0
undecanedioic acid	0.0	0.0	0.0	0.0	0.0	0.0	1.7	0.0
dodecanedioic acid	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1,11-undecanedicarboxylic acid	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1,12-dodecanedicarboxylic acid	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
sum	*202*	*127*	*847*	*1082*	*2273*	*286*	*746*	*227*
di/mono ratio	*1.530*	*0.121*	*0.903*	*1.703*	*0.799*	*0.960*	*0.593*	*0.115*

Table S5. Gas phase concentrations (µg mg^{-1}EC) for POC.

Aromatic acids (gas phase)	**L-1a**	**L-1b (VOC)**	**L-2a**	**L-2b (VOC)**	**L-3a (TOL)**	**L-3b (TOL)**	**D-1**	**D-2 (VOC)**
phenylacetic acid	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
o-toluic	6.4	656.5	79.2	98.2	73.0	5.5	26.6	35.5
m-toluic	2.2	85.8	35.8	15.7	30.9	3.2	13.4	51.7
p-toluic	17.9	913.2	288.4	201.2	238.2	19.7	89.0	267.3
2,6-dimethylbenzoic acid	0.0	156.7	0.0	8.4	0.0	0.0	0.0	377.9
2,5-dimethylbenzoic acid	3.1	406.4	54.4	44.2	75.1	8.1	19.4	378.1
2,4-dimethylbenzoic acid	1.6	56.1	16.7	11.1	25.6	0.0	10.4	24.9
3,5-dimethylbenzoic acid	0.0	55.2	0.0	53.5	0.0	1.7	0.0	0.0
3,4-dimethylbenzoic acid	3.9	1685.1	64.9	68.7	46.2	5.8	0.0	1235.2
2,3-dimethoxybenzoic acid	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2,6-dimethoxybenzoic acid	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2,5-dimethoxybenzoic acid	0.4	0.0	0.0	21.9	0.0	0.0	0.0	0.0
phthalic acid	29.9	327.6	179.9	129.5	303.7	6.4	18.8	129.6
isophthalic acid	0.0	4.2	206.0	65.3	114.1	1.5	482.1	57.9
dimethylbenzoic sum	9	2360	136	186	147	16	30	2016
sum	*65*	*4347*	*925*	*717*	*907*	*52*	*660*	*2558*

In general, many of the POC analyzed in this study showed significant variability across all experiments. The longer chain carboxylic acids do generally decrease in abundance, and diacid compounds such as 1,12-dodecanedicarboxylic acid (C_{14}; tetradecanedioic acid) and 1,11-undecanedicarboxylic acid (C_{13}; tridecanedioic acid) were not detected in the majority of experiments. Photochemical decomposition of longer chain unsaturated and/or polyaromatic compounds is observed in some cases. For example, the concentration of cis-9-octadecenoic (oleic) acid (a known precursor of nonanoic acid) does decrease in light exposures, relative to dark (Kawamura and Gagosian, 1987; Fraser et al., 2003).

Table S6. Particle phase concentrations (μg mg^{-1}EC) for POC.

Alkanoic acids (particle phase)	L-1a	L-1b (VOC)	L-2a	L-2b (VOC)	L-3a (TOL)	L-3b (TOL)	D-1	D-2 (VOC)
hexanoic acid	3.2	49.0	8.4	35.8	0.0	61.6	307.1	44.1
heptanoic acid	48.9	634.3	200.5	708.0	6537.5	1683.7	100.1	57.7
octanoic acid	7.0	24.7	10.0	22.2	4.2	30.2	49.8	37.5
nonanoic acid	10.0	32.3	27.0	44.5	7.2	46.0	61.1	88.4
decanoic acid	1.3	12.4	7.4	16.6	0.2	12.5	14.1	32.9
undecanoic acid	1.9	2.1	0.0	0.7	0.0	0.0	0.0	0.0
myristoleic acid	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
myristic acid	1.4	12.9	11.8	44.1	4.3	14.9	26.0	0.0
pentadecanoic acid	2.2	8.8	3.9	11.3	0.0	8.2	60.9	0.0
palmitic acid	17.4	118.9	63.3	75.7	121.6	136.3	216.5	114.2
isostearic acid	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
traumatic acid	0.4	5.5	0.0	2.6	0.0	0.0	0.0	0.0
oleic acid	0.3	62.1	145.5	3.5	132.4	89.5	145.3	77.2
elaidic acid	0.0	4.2	0.0	0.0	0.0	0.0	0.0	0.0
stearic acid	16.2	61.7	42.6	66.3	61.4	96.0	200.6	11.8
nonadecanoic acid	0.0	196.0	908.6	0.0	353.9	307.6	452.2	663.7
eicosanoic acid	0.0	4.2	0.0	0.0	0.0	0.0	6.8	0.0
heneicosanoic acid	0.0	9.8	0.0	0.2	0.0	0.0	0.0	0.0
docosanoic acid	0.0	5.9	0.0	0.0	0.0	0.0	0.0	0.0
tetracosanoic acid	0.5	0.0	0.0	5.1	0.0	0.0	0.0	0.0
sum	*111*	*1245*	*1429*	*1036*	*7223*	*2486*	*1640*	*1127*
Alkanedioic acids (particle phase)	**L-1a**	**L-1b (VOC)**	**L-2a**	**L-2b (VOC)**	**L-3a (TOL)**	**L-3b (TOL)**	**D-1**	**D-2 (VOC)**
oxalic acid	0.0	45.1	0.0	183.7	0.0	0.0	0.0	0.0
malonic acid	0.0	0.0	0.0	15.4	0.0	0.0	0.0	0.0
me-malonic	0.0	0.0	0.0	2.8	0.0	0.0	0.0	0.0
maleic acid	0.0	2188.6	542.0	367.2	16408.3	6663.2	0.0	121.1
succinic acid	180.9	1541.0	1349.1	179.8	600.2	463.7	157.0	299.7
me-succinic acid	23.4	329.5	184.5	208.5	188.4	104.8	23.6	52.0
glutaric acid	0.0	9.0	26.3	75.6	0.0	0.0	0.0	0.0
2-methylglutaric	0.0	14.6	0.0	0.9	0.0	0.0	0.0	0.0
3-methylglutaric acid	11.9	0.0	0.0	14.1	0.0	0.0	0.0	0.0
hexanedioic (adipic) acid	0.4	6.5	0.0	20.7	0.0	0.0	0.0	0.0
3-methyladipic acid	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
heptanedioic (pimelic) acid	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
suberic acid	0.0	3.4	0.0	2.5	0.0	0.0	0.0	0.0
azelaic acid	0.0	0.0	0.0	4.5	0.0	0.0	0.0	172.9
sebacic acid	0.0	7.3	0.0	0.0	26.6	27.2	0.0	0.0
undecanedioic acid	0.0	0.7	0.0	0.2	0.0	0.0	0.0	0.0
dodecanedioic acid	0.0	0.9	0.0	0.0	0.0	0.0	0.0	0.0
1,11-undecanedicarboxylic acid	0.0	6.2	0.0	0.0	0.0	0.0	0.0	0.0
1,12-dodecanedicarboxylic acid	0.0	8.8	0.0	0.0	0.0	4.2	0.0	10.4
sum	*217*	*4162*	*2102*	*1076*	*11224*	*7263*	*181*	*656*
di/mono ratio	*1.957*	*3.343*	*1.471*	*1.038*	*2.385*	*2.921*	*0.110*	*0.582*

Table S7. Particle phase concentrations (μg mg^{-1}EC) for POC.

Aromatic acids (particle phase)	**L-1a**	**L-1b (VOC)**	**L-2a**	**L-2b (VOC)**	**L-3a (TOL)**	**L-3b (TOL)**	**D-1**	**D-2 (VOC)**
phenylacetic acid	0.0	12.9	0.0	26.4	0.0	0.0	0.0	0.0
o-toluic	9.0	311.6	5.1	15.2	4.7	5.9	10.1	12.7
m-toluic	5.2	22.8	12.2	6.1	7.5	5.1	11.7	21.0
p-toluic	10.4	168.7	23.4	22.8	11.6	9.9	16.5	28.5
2,6-dimethylbenzoic acid	0.0	43.6	0.0	51.2	0.0	18.5	32.2	53.8
2,5-dimethylbenzoic acid	539.2	1825.5	0.0	486.2	0.0	1327.8	3206.9	2656.5
2,4-dimethylbenzoic acid	13.8	0.0	0.0	23.1	17.0	0.0	0.0	0.0
3,5-dimethylbenzoic acid	0.0	0.0	0.0	69.2	0.0	0.0	0.0	0.0
3,4-dimethylbenzoic acid	0.0	153.9	0.0	14.0	0.0	0.0	0.0	70.6
2,3-dimethoxybenzoic acid	0.0	0.0	72.4	0.0	0.0	0.0	0.0	0.0
2,6-dimethoxybenzoic acid	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2,5-dimethoxybenzoic acid	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
phthalic acid	165.7	7434.2	285.5	630.1	324.3	257.4	0.0	491.8
isophthalic acid	71.0	2500.4	115.6	0.0	0.0	1465.9	2128.6	3957.7
dimethylbenzoic sum	553	2023	0	644	17	1346	3239	2781
sum	*814*	*12473*	*514*	*1344*	*365*	*3091*	*5406*	*7293*

Phthalic acid may also be the photooxidation product of larger molecular weight semi-volatile PAHs that are less abundant than naphthalene (Jang and McDow, 1997). It is clear from the L-1 (DE) or L-2 (DE + OH) experiments with (L-1b, L-2b) and without (L-1a, L-2a) VOC addition, that the initial concentration of possible precursors (e.g. naphthalene, o-xylene, 1,2-diethylbenzene) does ultimately impact the concentration of such proposed SOA tracers.

In addition to condensation of oxygenated compounds formed via photochemical reactions, heterogeneous reactions on DPM during aging can lead to a more polar composition (Lee et al., 2004; Kroll and Seinfeld, 2008). These reactions can be catalyzed by indigenous sulfuric acid (or HNO_3), which is dependent upon the initial fuel composition and is present in the particle phase DE (Jang et al., 2002; Zielinska et al., 2009). The ionic analysis (sulfate, nitrate) of DPM did not provide any discernable correlation between SOA production and particle bound nitrates or sulfates, which may have contributed to particle acidity. However, the acids detected in this study can also contribute to an acidic environment in the particle phase allowing proton (H) exchange and increases in reaction rates and chemical transformations, which would otherwise be thermodynamically hindered (Barsanti and Pankow, 2006). For example, the presence of maleic, phthalic, and succinic acids (pKa = 1.9, 2.9, 4.2; respectively) at relatively high concentrations (Table 3) can result in hydrogen donation to reduce activation energies in otherwise unlikely reactions (Carey and Sundberg, 1990; Johnson et al., 2005).

Table S8. Chamber conditions for 2006 experiments.

Name	Date	Run Description	Post-Injection DPM ($\mu g\ m^{-3}$)	NO_x (ppb)	HCHO Max, Mean, Median (ppb)	Ozone Max. (ppb)
D-1	05/31/06	DE in dark	29	36	ND [A]	ND
D-2	06/01/06	DE+N_2O_5 in dark	28	333	3	442
L-1a	06/08/06	DE+Sun	44	77	ND	22
L-1b	06/02/06	DE+Sun+VOC	49	82	30	188
L-2a	06/05/06	DE+Sun+OH	40	27	252,37,13	147
L-2b	06/07/06	DE+Sun+OH+VOC	29	58	263,58,32	251
L-3a	06/06/06	DE+Toluene	32	25	37,13,10	112
L-3b	06/09/06	DE+Toluene	40	98	20,10,10	185

[A] ND, not detected

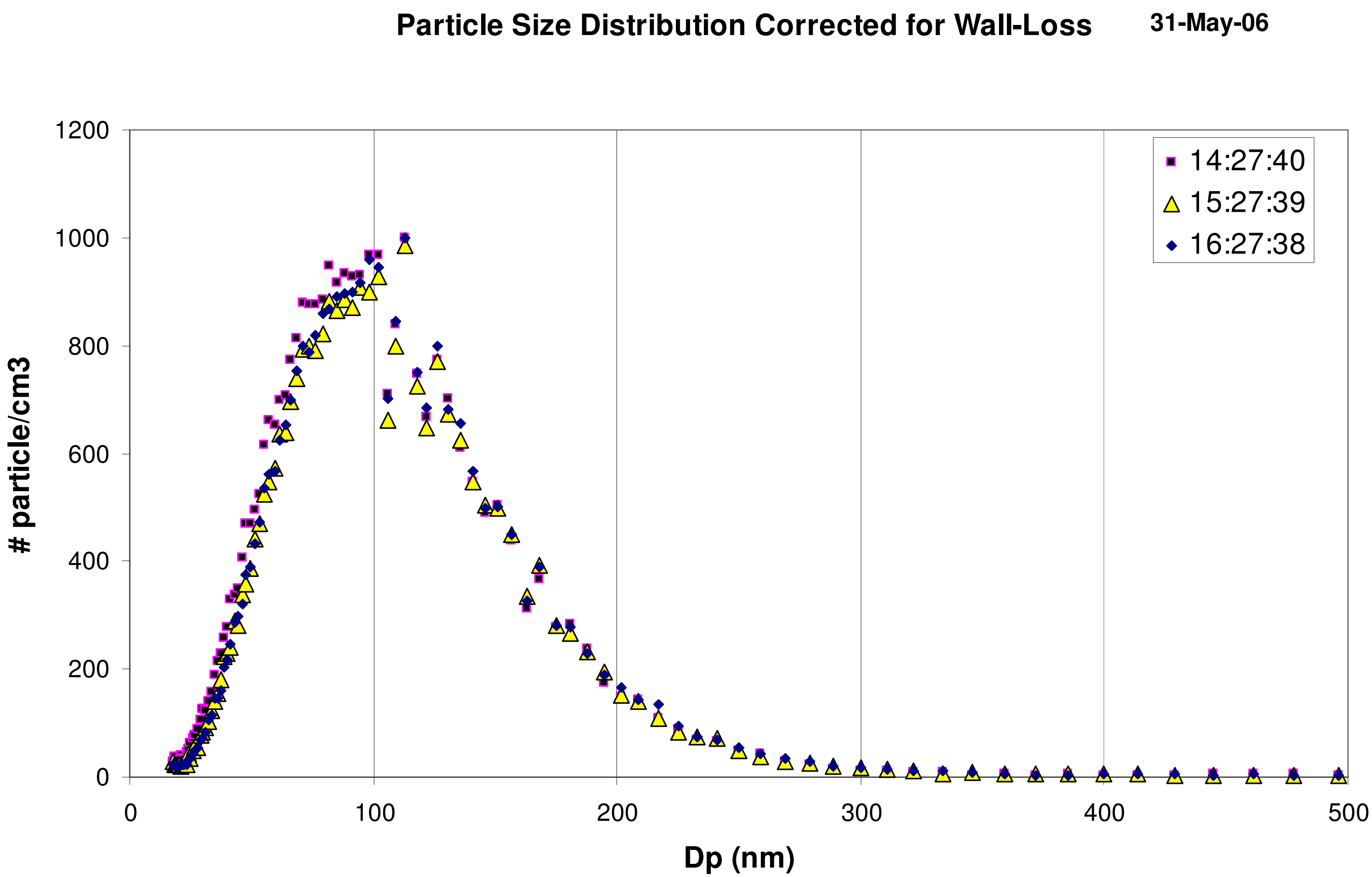

Figure S1. Corrected particle profile for diesel in dark aging experiment at 0,1,and 2 hours.

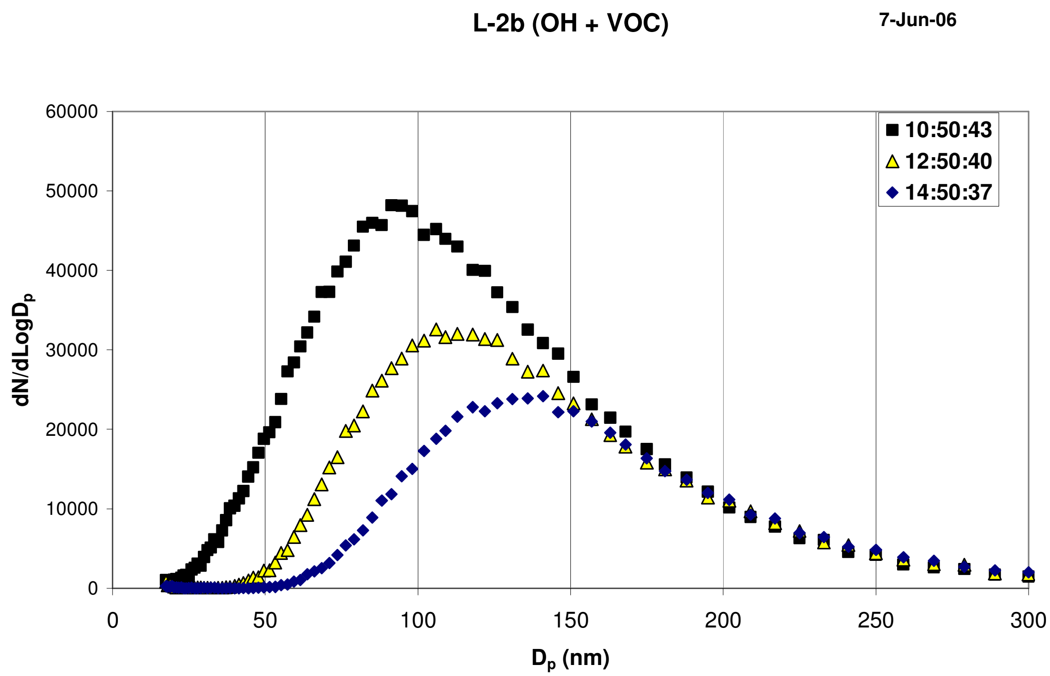

Figure S2. Non-corrected particle profiles for diesel in light with OH + VOC aging experiment L-2b on 06/07/06.

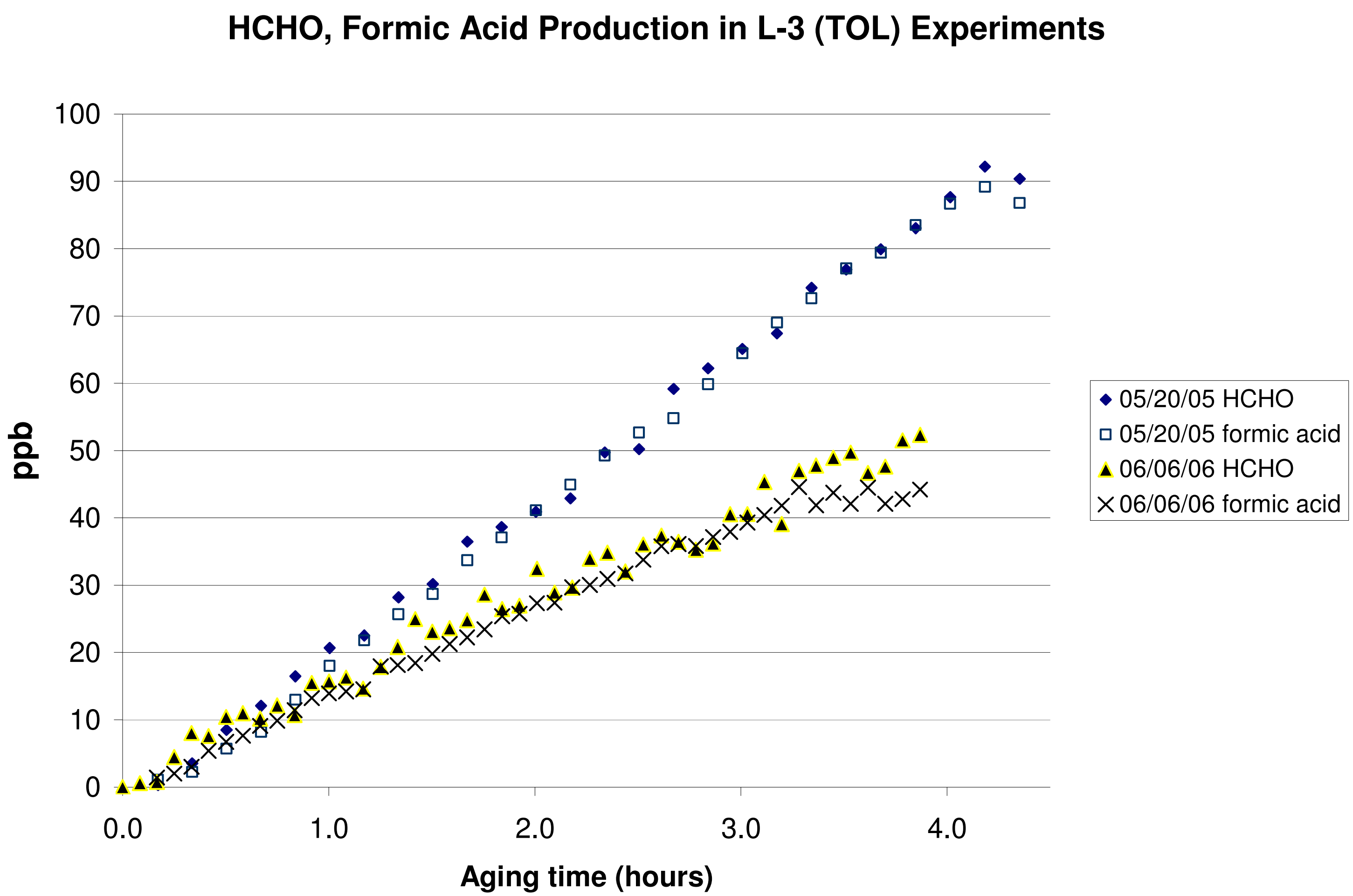

Figure S3. HCHO and formic acid production measured by FTIR and corrected for loss for L-3a (06/06/06) and L-3d (05/20/05).