

Supplemental Material

VOC Removal from Manure Gaseous Emissions with UV Photolysis and UV-TiO₂ Photocatalysis

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Table S1. UV₁₈₅₊₂₅₄+TiO₂: summary of mass removal rates, measured gas concentrations in UV-treated gas, and percent VOC reduction.

Compound name	Treatment time (sec) / measured energy dose at 254 nm (J)										Mass Removal Rate (ng/J)
	2.5 sec		19 sec		37 sec		56 sec		112 sec		
	0.02 J		2.90 J		5.64 J		8.54 J		17.1 J		
	C_{gas}	R (%)	C_{gas}	R (%)	C_{gas}	R (%)	C_{gas}	R (%)	C_{gas}	R (%)	
Methyl mercaptan	0.755	22.1	0.297	70.9	0.308	78.8	0.151	98.0	MDL	99.8	4.72
Ethyl mercaptan	1.55	25.2	0.853	66.0	0.899	73.2	0.563	97.9	MDL	99.7	14.6
Dimethyl sulfide	0.428	23.5	0.267	63.6	0.273	67.4	0.187	92.2	MDL	99.6	4.94
Butyl mercaptan	0.224	29.3	0.112	65.8	0.121	75.3	0.073	94.5	MDL	99.5	8.68
Acetic acid	0.554	-16.0	0.227	51.4	0.212	61.2	0.113	80.1	0.071	93.1	11.6
Propanoic acid	0.456	7.16	0.198	59.9	0.185	65.7	0.084	85.0	0.042	96.7	8.65
Butyric acid	0.543	19.8	0.210	56.7	0.280	63.1	0.114	83.8	0.074	97.1	15.7
Isovaleric acid	1.90	21.1	0.563	51.7	1.07	57.3	0.287	80.2	0.133	97.8	49.2
p-Cresol	3.00	25.4	0.637	64.6	1.11	72.8	0.143	91.7	0.019	99.9	78.9
Note: The unit for C_{gas} is ng mL ⁻¹ ; R refers to % reduction.											

Note: The unit for *C_{gas}* is ng mL⁻¹; *R* refers to % reduction.

Table S2. UV₁₈₅₊₂₅₄: summary of mass removal rates, measured gas concentrations in UV-treated gas, and percent VOC reduction.

Compound name	Treatment time (sec) / measured energy dose at 254 nm (J)										Mass Removal Rate (ng/J)
	2.5 sec		19 sec		37 sec		56 sec		112 sec		
	0.02 J		2.90 J		5.64 J		8.54 J		17.1 J		
	<i>C_{gas}</i>	<i>R</i> (%)	<i>C_{gas}</i>	<i>R</i> (%)	<i>C_{gas}</i>	<i>R</i> (%)	<i>C_{gas}</i>	<i>R</i> (%)	<i>C_{gas}</i>	<i>R</i> (%)	
Methyl mercaptan	0.865	8.26	0.426	46.9	0.360	57.0	0.247	80.0	0.215	90.7	5.23
Ethyl mercaptan	1.68	15.3	1.06	43.3	0.919	50.2	0.761	82.0	0.622	93.7	15.6
Dimethyl sulfide	0.455	15.9	0.356	34.3	0.296	46.4	0.218	84.1	0.187	91.6	4.49
Butyl mercaptan	0.239	22.4	0.128	54.8	0.113	65.6	0.0820	87.7	0.0681	98.6	9.37
Acetic acid	0.720	-53.6	0.526	-26.5	0.516	-36.2	0.622	-59.7	0.874	-88.4	-
Propanoic acid	0.571	-17.9	0.421	8.06	0.398	4.53	0.441	-7.37	0.440	10.4	-
Butyric acid	0.650	2.12	0.378	9.25	0.428	8.60	0.448	-9.69	0.438	37.2	-
Isovaleric acid	2.20	8.17	0.970	10.9	1.30	8.73	1.20	-8.43	1.49	39.0	-
p-Cresol	3.40	15.6	0.701	61.0	0.376	76.9	0.460	70.9	MDL	99.1	98.0
Note: The unit for <i>C_{gas}</i> is ng mL ⁻¹ ; <i>R</i> refers to % reduction											

Note: The unit for *C_{gas}* is ng mL⁻¹; *R* refers to % reduction.

Table S3. UV₂₅₄+TiO₂: summary of mass removal rates, measured gas concentrations in UV-treated gas, and percent VOC reduction.

Compound name	Treatment time (sec) / measured energy dose at 254 nm (J)										Mass Removal Rate (ng/J)
	2.5 sec		19 sec		37 sec		56 sec		112 sec		
	0.02 J		2.90 J		5.64 J		8.54 J		17.1 J		
	C_{gas}	R (%)	C_{gas}	R (%)	C_{gas}	R (%)	C_{gas}	R (%)	C_{gas}	R (%)	
Methyl mercaptan	0.931	-0.13	0.334	66.0	0.348	68.2	0.198	89.2	0.146	99.3	4.43
Ethyl mercaptan	1.81	5.75	0.916	58.6	0.462	60.1	0.664	89.8	0.543	99.5	13.6
Dimethyl sulfide	0.484	7.70	0.261	58.4	0.157	60.8	0.188	92.1	0.160	99.1	4.32
Butyl mercaptan	0.267	9.88	0.127	57.4	0.081	57.3	0.080	89.0	MDL	99.5	9.46
Acetic acid	0.685	-45.6	0.166	59.2	0.219	62.6	0.088	87.0	0.080	91.0	11.3
Propanoic acid	0.586	-21.1	0.124	58.5	0.245	63.0	0.073	87.8	0.038	97.5	8.41
Butyric acid	0.716	-8.7	0.154	46.2	0.243	59.8	0.110	85.1	0.070	97.7	16.2
Isovaleric acid	2.33	2.62	0.463	31.4	0.697	52.2	0.289	79.9	0.151	97.0	49.9
p-Cresol	3.64	9.51	1.15	40.5	0.837	53.8	0.466	70.6	0.047	99.2	111
Note: The unit for C_{gas} is ng mL ⁻¹ ; R refers to % reduction.											

Note: The unit for *C_{gas}* is ng mL⁻¹; *R* refers to % reduction.

Table S4. UV₂₅₄: summary of mass removal rates, measured gas concentrations in UV-treated gas, and percent VOC reduction.

Compound name	Treatment time (sec) / measured energy dose at 254 nm (J)										Mass Removal Rate (ng/J)
	2.5 sec		19 sec		37 sec		56 sec		112 sec		
	0.02 J		2.90 J		5.64 J		8.54 J		17.1 J		
	C_{gas}	R (%)	C_{gas}	R (%)	C_{gas}	R (%)	C_{gas}	R (%)	C_{gas}	R (%)	
Methyl mercaptan	-	-	0.297	3.8	0.632	78.8	0.534	25.7	0.525	51.3	1.20
Ethyl mercaptan	-	-	0.853	14.0	1.20	73.2	1.48	24.7	1.17	53.4	4.04
Dimethyl sulfide	-	-	0.267	10.6	0.388	67.4	0.475	17.7	0.306	57.8	1.48
Butyl mercaptan	-	-	0.112	25.8	0.170	75.3	0.152	36.7	0.095	86.5	3.76
Acetic acid	-	-	0.227	-3.79	0.403	61.2	0.462	-15.8	0.600	-26.4	-
Propanoic acid	-	-	0.198	5.23	0.395	65.7	0.421	-2.25	0.452	7.83	-
Butyric acid	-	-	0.210	2.13	0.454	63.1	0.407	1.72	0.484	29.6	-
Isovaleric acid	-	-	0.563	-0.07	1.42	57.3	1.07	4.45	1.77	27.0	-
p-Cresol	-	-	0.637	19.1	1.27	72.8	0.973	37.4	0.751	81.6	94.0
Note: The unit for C_{gas} is ng mL ⁻¹ ; R refers to % reduction.											

Note: The unit for *C_{gas}* is ng mL⁻¹; *R* refers to % reduction.

Table S5. UV₂₅₄₊₁₈₅ + TiO₂. Linearity of percent conversion (y) and measured light energy (x) dosage at 254 nm.

Compound name	y ₁ = percent conversion (R, %)			y ₂ = mass removed (ng J ⁻¹)		
	y ₁ =m ₁ ·x+b ₁		R ₁ ²	y ₂ =m ₂ ·x+b ₂		R ₂ ²
	m ₁	b ₁		m ₂	b ₂	
Methyl mercaptan	8.46	34.0	0.856	4.72	0.658	0.941
Ethyl mercaptan	1.27	32.0	0.893	14.6	-0.527	0.960
Dimethyl sulfide	1.19	31.0	0.867	4.94	-1.24	0.985
Butyl mercaptan	1.15	37.7	0.840	8.68	-1.26	0.971
Acetic acid	10.6	2.90	0.788	11.6	-1.81	0.960
Propanoic acid	1.36	18.9	0.804	8.65	-2.86	0.949
Butyric acid	1.14	22.0	0.959	15.7	-7.50	0.887
Isovaleric acid	1.11	16.8	0.996	49.2	-34.3	0.895
p-Cresol	1.23	25.2	0.989	78.9	-9.63	0.978

Note: Experimental conditions: 25 mg TiO₂ for UV₁₈₅₊₂₅₄+TiO₂ treatment; 300 mL/min airflow; T=25 °C; dry air. Percent conversion = m₁ × (light energy dose at 254 nm) + b₁; mass removed = m₂ × (light energy dose at 254 nm) + b₂

Table S6. Reproducibility of the effect of light energy dose on UV treatment: ranges of RSDs (%).

Compound name	UV ₁₈₅₊₂₅₄ +TiO ₂			UV ₁₈₅₊₂₅₄ ; no catalyst			UV ₂₅₄ +TiO ₂			UV ₂₅₄ ; no catalyst		
	Avg. RSD	Max RSD	Min RSD	Avg. RSD	Max RSD	Min RSD	Avg. RSD	Max RSD	Min RSD	Avg. RSD	Max RSD	Min RSD
Methyl mercaptan	4.13 ±(4.43)	11.3	0.00	5.01 ±(4.98)	13.0	0.455	3.52 ±(2.52)	6.22	0.0737	2.53 ±(1.48)	4.23	1.10
Ethyl mercaptan	4.0 ±(7.15)	16.8	0.00	6.28 ±(5.50)	15.4	1.19	4.35 ±(2.79)	7.48	0.870	2.58 ±(1.64)	5.02	1.57
Dimethyl sulfide	3.40 ±(2.70)	7.05	0.00	4.04 ±(4.35)	11.3	0.143	5.73 ±(3.20)	9.92	2.16	1.95 ±(0.808)	2.86	0.963
Butyl mercaptan	6.36 ±(7.61)	16.2	0.00	8.63 ±(6.01)	16.9	0.934	4.52 ±(3.39)	9.09	0.00	4.16 ±(2.18)	6.83	1.49
Acetic acid	4.37 ±(3.89)	11.2	1.79	1.76 ±(1.87)	5.09	0.707	2.91 ±(2.82)	7.84	0.816	3.21 ±(1.86)	5.02	1.28
Propanoic acid	4.68 ±(2.98)	7.90	0.637	1.62 ±(1.39)	4.06	0.677	2.21 ±(0.497)	2.70	1.42	2.51 ±(1.17)	3.99	1.54
Butyric acid	4.07 ±(3.40)	9.58	0.720	2.14 ±(2.15)	5.73	0.372	1.57 ±(0.762)	2.52	0.456	3.07 ±(1.63)	4.73	1.18
Isovaleric acid	1.76 ±(1.80)	4.77	0.0161	2.48 ±(2.34)	6.07	0.403	1.53 ±(0.596)	2.16	0.733	2.69 ±(1.52)	4.36	1.28
p-Cresol	6.37 ±(8.55)	20.9	0.273	2.14 ±(1.10)	2.99	0.295	3.29 ±(1.53)	4.78	1.07	5.00 ±(5.07)	12.3	0.496

Table S7. Reproducibility of the effect of relative humidity on UV treatment: ranges of RSDs (%).

Compound name	UV ₁₈₅₊₂₅₄ +TiO ₂			UV ₁₈₅₊₂₅₄ ; no catalyst			UV ₂₅₄ +TiO ₂			UV ₂₅₄ ; no catalyst		
	Avg. RSD	Max RSD	Min RSD	Avg. RSD	Max RSD	Min RSD	Avg. RSD	Max RSD	Min RSD	Avg. RSD	Max RSD	Min RSD
Methyl mercaptan	9.33±(3.75)	15.7	6.76	6.34±(2.28)	9.81	3.81	6.85±(3.51)	10.1	2.68	4.41±(2.56)	7.96	1.75
Ethyl mercaptan	6.15±(2.90)	8.5	2.14	4.59±(2.12)	6.61	1.48	5.71±(3.68)	12.0	2.41	3.36±(2.18)	5.51	0.122
Dimethyl sulfide	5.76±(1.88)	7.9	2.90	5.79±(1.29)	8.07	4.99	5.72±(3.39)	9.89	1.31	2.85±(1.93)	5.13	0.690
Butyl mercaptan	10.1±(6.40)	16.3	1.24	8.77±(4.31)	15.0	3.91	5.64±(3.46)	9.65	1.86	4.62±(2.41)	7.48	0.853
Acetic acid	6.44±(3.16)	11.2	3.27	4.32±(2.94)	8.19	0.846	5.37±(6.70)	16.7	0.317	4.74±(2.52)	7.56	2.10
Propanoic acid	6.85±(2.91)	10.9	3.08	8.05±(4.19)	13.7	2.30	5.16±(3.21)	9.77	1.43	6.45±(4.29)	10.8	0.888
Butyric acid	6.35±(2.13)	8.75	3.32	9.25±(4.96)	16.1	3.51	6.62±(4.41)	10.7	0.358	6.08±(4.93)	13.9	0.770
Isovaleric acid	9.37±(1.43)	11.5	7.68	10.7±(4.50)	16.4	4.85	5.88±(4.69)	13.2	1.67	6.49±(3.00)	10.7	2.78
p-Cresol	9.10±(3.83)	13.3	5.05	8.32±(4.46)	14.4	2.75	5.56±(2.55)	9.07	2.72	5.29±(3.22)	9.7	2.47

Table S8. Reproducibility of the effect of temperature on UV treatment: ranges of RSDs (%).

Compound name	UV ₁₈₅₊₂₅₄ +TiO ₂			UV ₁₈₅₊₂₅₄ ; no catalyst			UV ₂₅₄ +TiO ₂			UV ₂₅₄ ; no catalyst		
	Avg. RSD	Max RSD	Min RSD	Avg. RSD	Max RSD	Min RSD	Avg. RSD	Max RSD	Min RSD	Avg. RSD	Max RSD	Min RSD
methyl mercaptan	4.72±(2.71)	7.23	0.27	5.99±(2.84)	8.58	0.791	3.34±(2.77)	8.40	0.864	3.34±(1.68)	6.26	1.84
ethyl mercaptan	6.08±(2.81)	8.99	1.48	6.57±(3.05)	8.82	0.737	3.44±(1.97)	5.87	0.743	1.46±(1.08)	2.48	0.122
dimethyl sulfide	2.70±(1.35)	4.99	1.41	3.78±(3.03)	7.92	0.55	4.10±(4.04)	11.1	1.23	3.26±(1.71)	6.68	2.15
butyl mercaptan	8.03±(1.75)	10.1	4.93	7.91±(3.72)	11.7	1.24	4.82±(3.05)	8.37	1.22	4.81±(2.95)	8.42	0.543
acetic acid	1.97±(1.14)	4.14	0.85	1.98±(1.28)	3.80	0.72	3.90±(4.60)	10.5	0.32	2.02±(0.67)	3.05	1.13
propanoic acid	2.25±(0.51)	2.98	1.50	1.81±(0.94)	3.08	0.375	1.94±(0.96)	3.28	1.10	1.58±(0.71)	2.46	0.576
butyric acid	2.35±(1.01)	3.51	0.92	2.87±(1.84)	6.18	0.780	2.24±(1.01)	3.65	1.29	1.91±(1.02)	3.06	0.649
isovaleric acid	2.36±(1.46)	4.85	0.43	3.34±(3.24)	9.68	1.07	2.69±(2.90)	8.41	0.295	2.44±(0.86)	3.23	0.817
p-Cresol	9.74±(5.23)	19.1	4.27	9.23±(7.64)	21.1	1.99	6.28±(3.84)	10.5	0.196	3.93±(1.41)	5.10	1.60

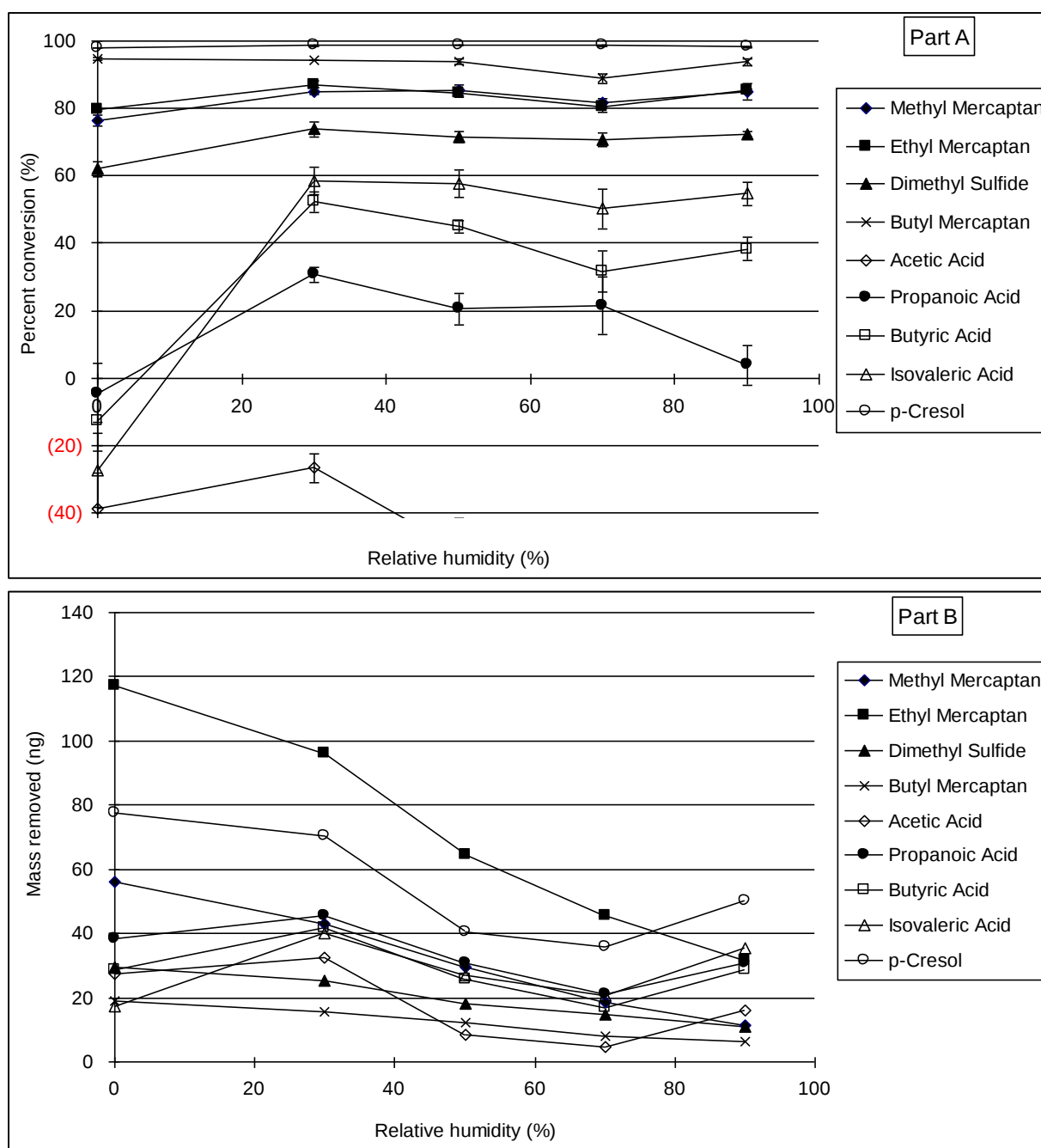


Fig. S1. Effect of RH (%) on Part A) percent conversion; Part B) mass removed (ng) of target odorous VOCs and treatment with $UV_{185+254}+TiO_2$. *Experimental conditions:* light intensity at 254 nm, 312 nm and 365 nm was 1.5, 0.230 and 0.084 $mW\ cm^{-2}$, respectively; 25 mg TiO_2 ; 400 $mL\ min^{-1}$ airflow; treatment time = 28 s; CAR/PDMS 85 μm ; 5 min sampling time; $T=25\ ^\circ C$.

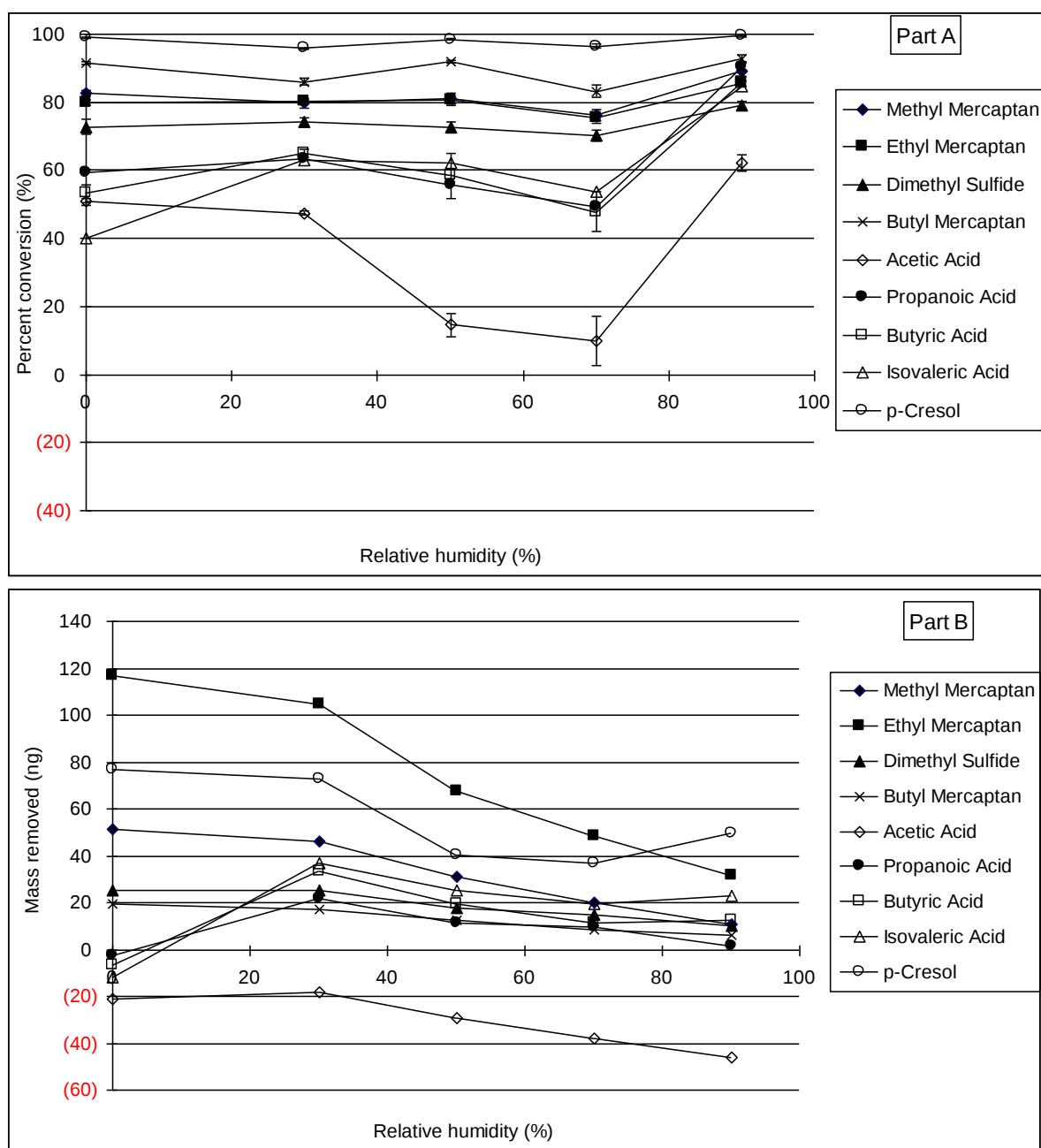


Fig. S2. Effect of RH (%) on Part A) percent conversion; Part B) mass removed (ng) of target odorous VOCs treatment with $UV_{185+254}$, no catalyst. Experimental conditions: light intensity at 254 nm, 312 nm and 365 nm was 1.5, 0.230 and 0.084 $mW\ cm^{-2}$, respectively; 25 mg TiO_2 ; 400 $mL\ min^{-1}$ airflow; treatment time = 28 s; CAR/PDMS 85 μm ; 5 min sampling time; $T=25\ ^\circ C$.

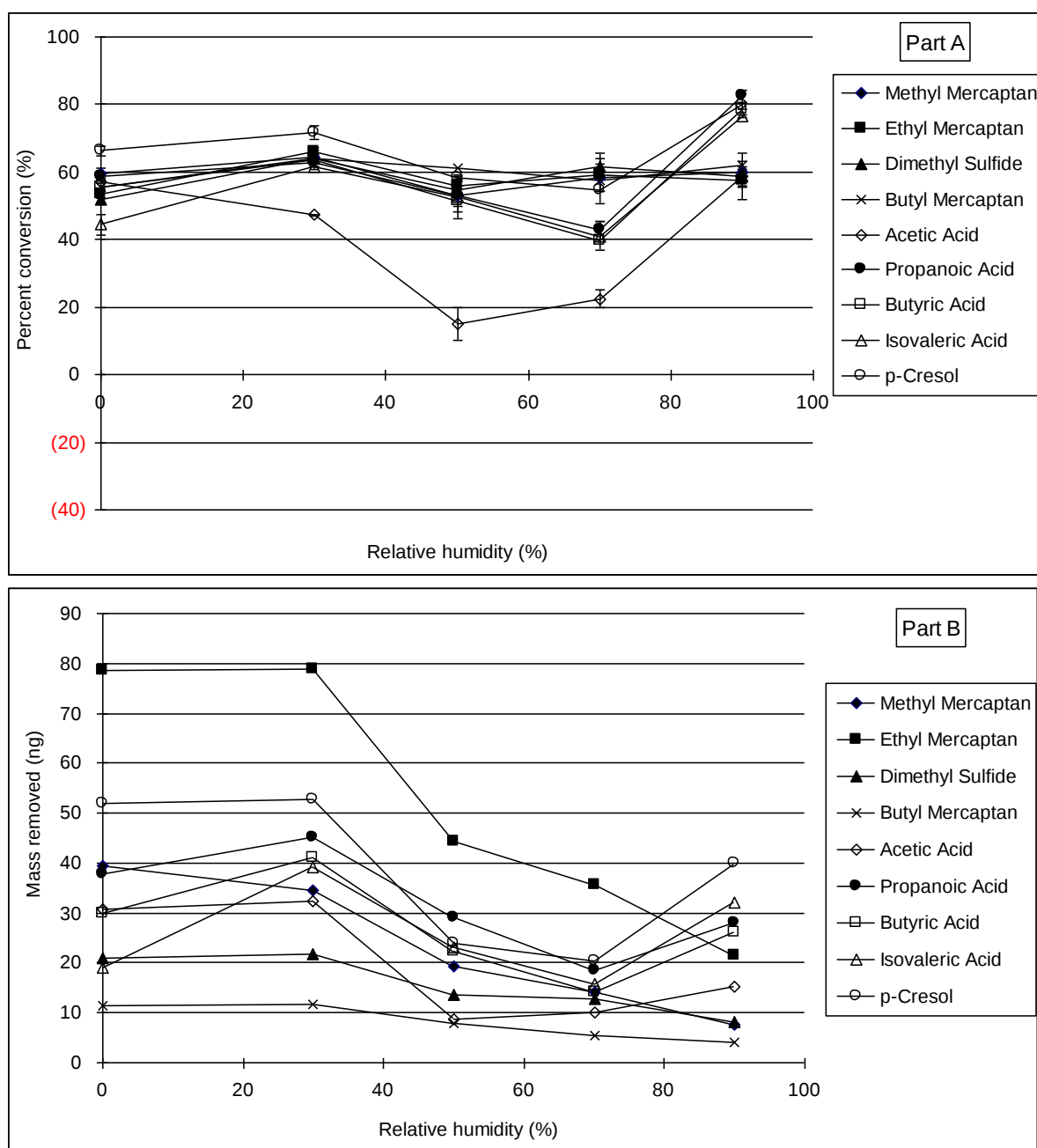


Fig. S3. Effect of RH (%) on Part A) percent conversion; Part B) mass removed (ng) of target odorous VOCs treatment with $UV_{254}+TiO_2$. Experimental conditions: light intensity at 254 nm, 312 nm and 365 nm was 1.5, 0.230 and 0.084 $mW\ cm^{-2}$, respectively; 25 mg TiO_2 ; 400 $mL\ min^{-1}$ airflow; treatment time = 28 s; CAR/PDMS 85 μm ; 5 min sampling time; $T=25\ ^\circ C$.

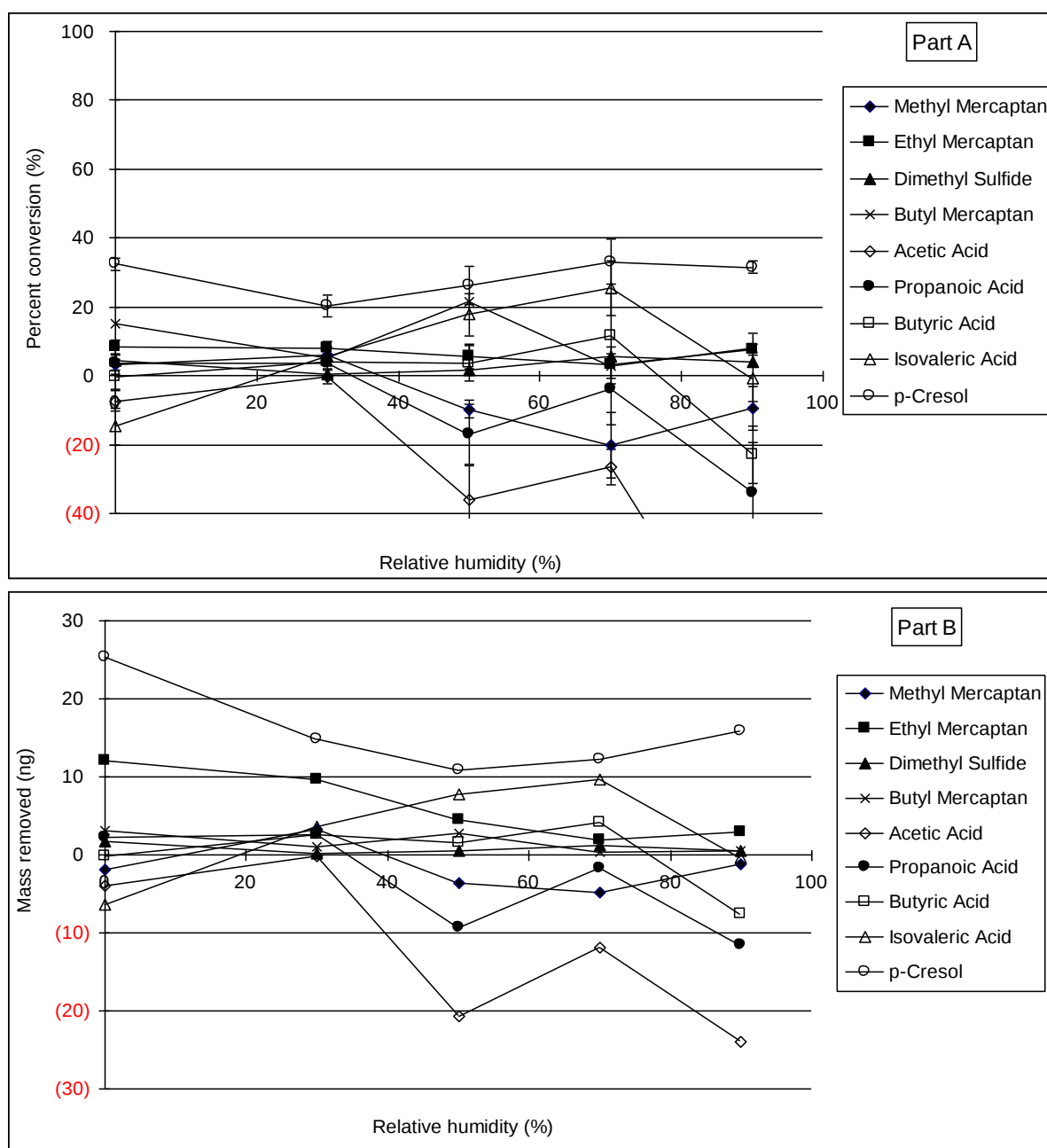


Fig. S4. Effect of RH (%) on Part A) percent conversion; Part B) mass removed (ng) of target odorous VOCs treated with UV₂₅₄, no catalyst. Experimental conditions: light intensity at 254 nm, 312 nm and 365 nm was 1.5, 0.230 and 0.084 mW cm⁻², respectively; 25 mg TiO₂; 400 mL min⁻¹ airflow; treatment time = 28 s; CAR/PDMS 85 μm; 5 min sampling time; T=25 °C.

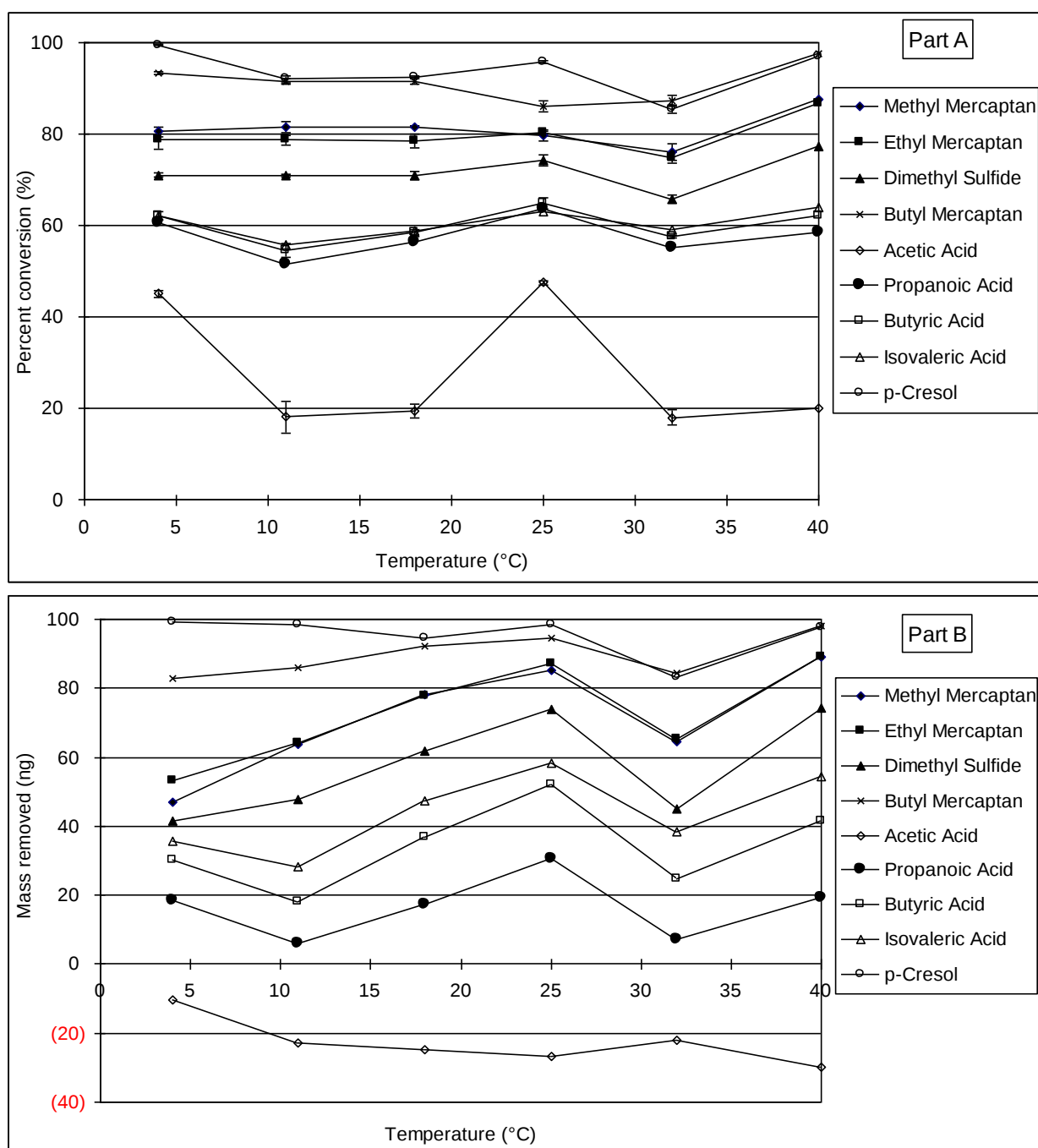


Fig. S5. Effects of air temperature on Part A) percent conversion; Part B) mass removed (ng) of target odorous VOCs treated with $UV_{185+254}+TiO_2$. Experimental conditions: light intensity at 254 nm, 312 nm and 365 nm was 1.5, 0.230 and 0.084 $mW\ cm^{-2}$, respectively; 25 mg TiO_2 ; 400 $mL\ min^{-1}$ airflow; treatment time = 28 s; CAR/PDMS 85 μm ; 5 min sampling time; RH=30 %.

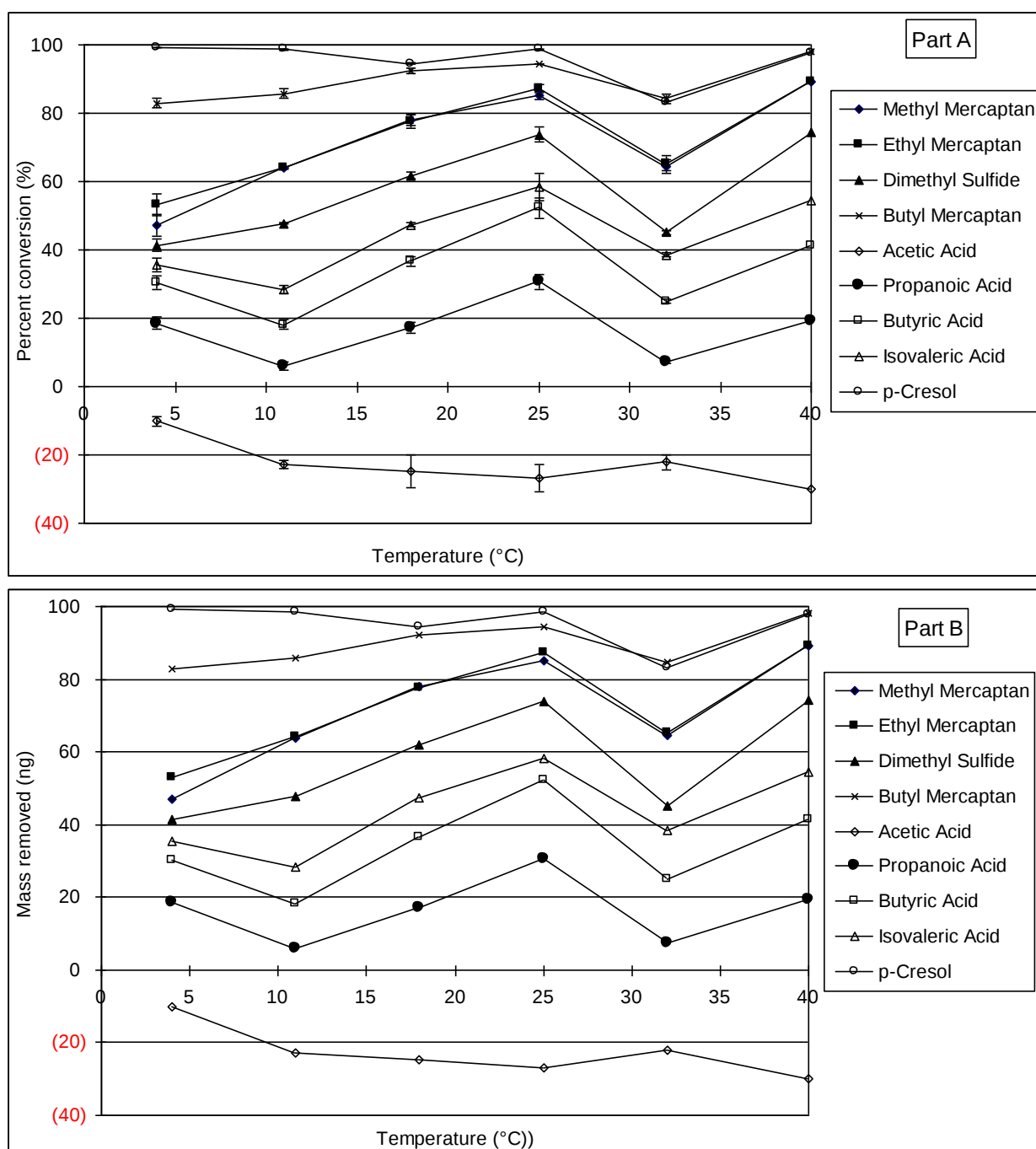


Fig. S6. Effects of air temperature on Part A) percent conversion; Part B) mass removed (ng) of target odorous VOCs treated with UV₁₈₅₊₂₅₄, no catalyst. Experimental conditions: light intensity at 254 nm, 312 nm and 365 nm was 1.5, 0.230 and 0.084 mW cm⁻², respectively; 25 mg TiO₂; 400 mL min⁻¹ airflow; treatment time = 28 s; CAR/PDMS 85 μm; 5 min sampling time; RH=30 %.

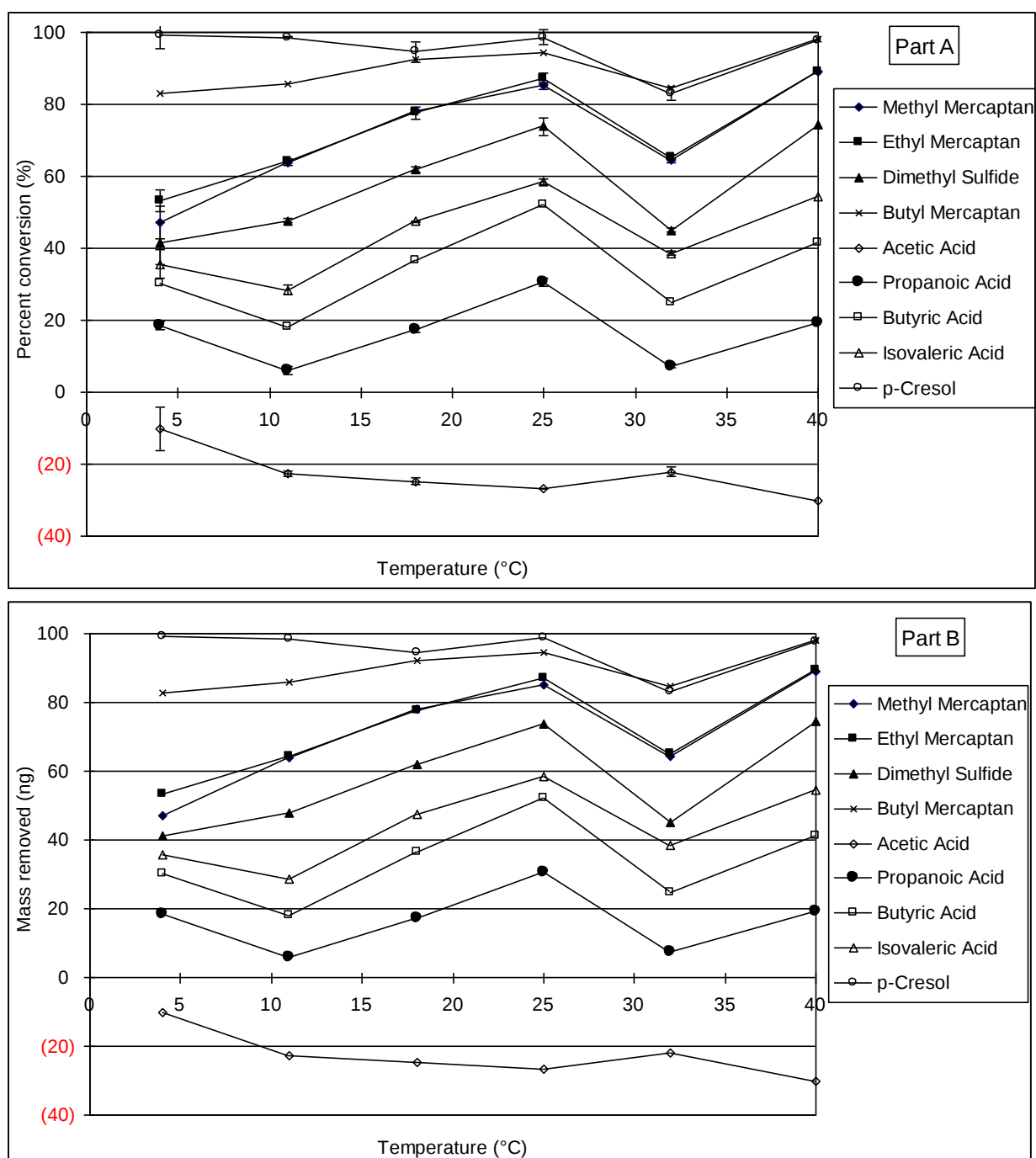


Fig. S7. Effects of air temperature on Part A) percent conversion; Part B) mass removed (ng) of target odorous VOCs treated with $UV_{254}+TiO_2$. Experimental conditions: light intensity at 254 nm, 312 nm and 365 nm was 1.5, 0.230 and 0.084 $mW\ cm^{-2}$, respectively; 25 mg TiO_2 ; 400 $mL\ min^{-1}$ airflow; treatment time = 28 s; CAR/PDMS 85 μm ; 5 min sampling time; RH=30 %.

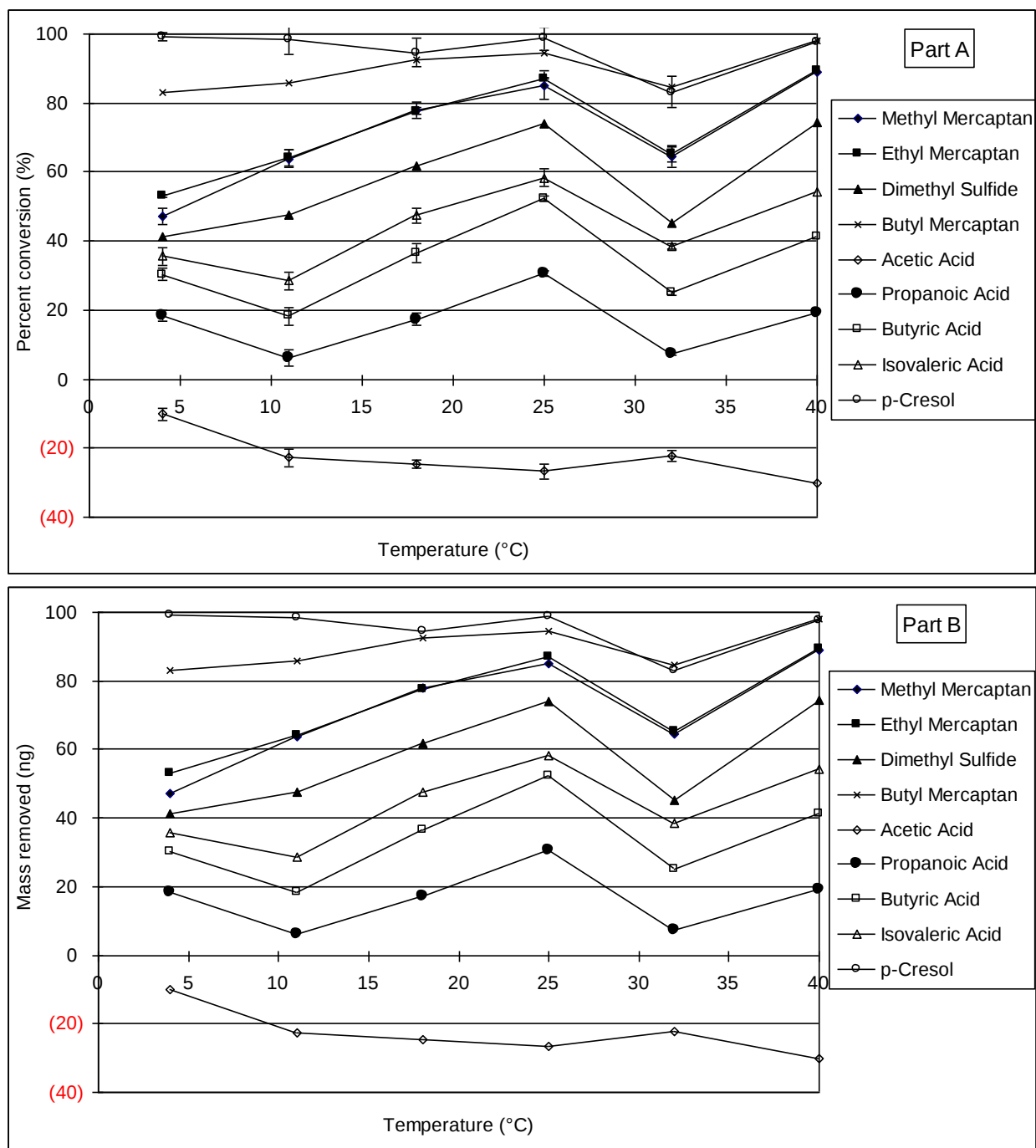


Fig. S8. Effects of air temperature on Part A) percent conversion; Part B) mass removed (ng) of target odorous VOCs treated with UV₂₅₄, no catalyst. Experimental conditions: light intensity at 254 nm, 312 nm and 365 nm was 1.5, 0.230 and 0.084 mW cm⁻², respectively; 25 mg TiO₂; 400 mL min⁻¹ airflow; treatment time = 28 s; CAR/PDMS 85 μm; 5 min sampling time; RH=30 %.

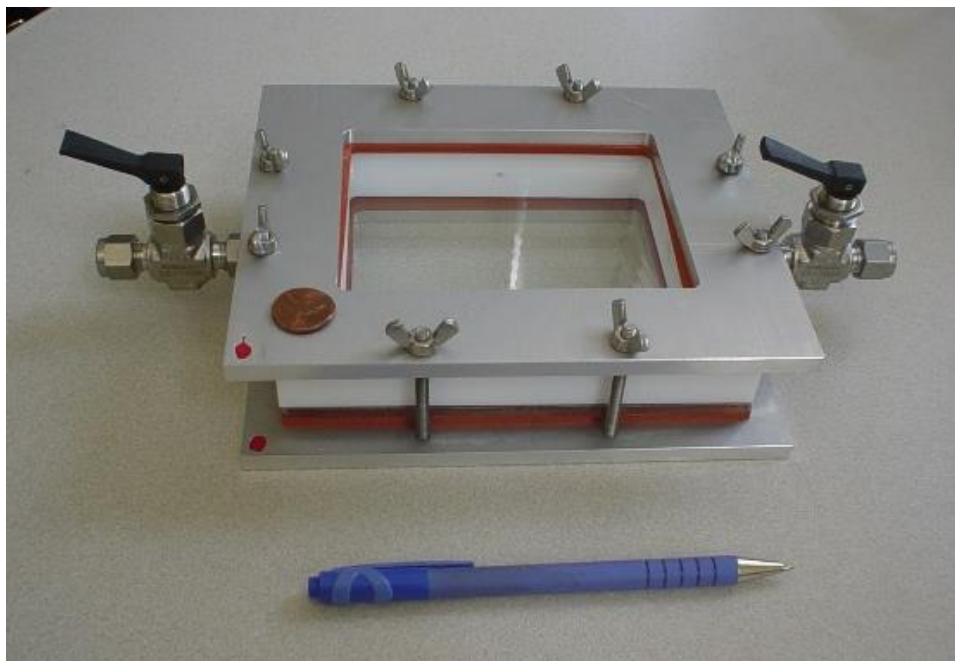


Fig. S9. Flow-through photoreactor used for lab-scale UV treatment of odorous VOCs at Iowa State University. The reactor walls in contact with VOCs are made of glass, quartz, Teflon,