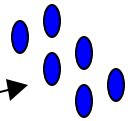
smog production

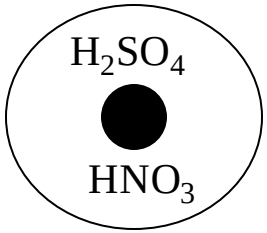
$NMHC + NO_x + h\nu \longrightarrow O_3$ + other pollutants



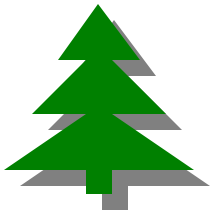
multiphase reactions

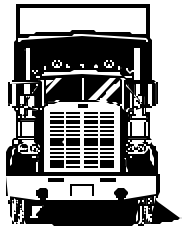
heterogeneous reactions

secondary organic aerosols



acidic aerosol





Measurement Techniques for Gas- and Particle- Phase Species

Real-Time Measurements

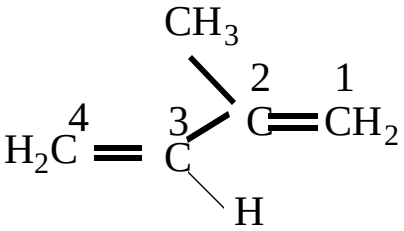
Proton-Transfer-Reaction Mass Spectrometry
On-line single particle measurements

Samplers for Gas-Phase Species

Sorbent tubes
Impingers
Mist Chamber

Samplers for Gas- and Particle- Phase Species

Denuder/Filter /Poyurethane foam



2-methyl-1,3-butadiene

Isoprene

OH·

Methyl vinyl ketone (32%)

Formaldehyde (63%)

Methacrolein (23%)

OH·

Glycolaldehyde (70%)

Methylglyoxal
+ Formaldehyde (30%)

OH·

Glyoxal
(20%)

Formaldehyde
(80%)

OH·

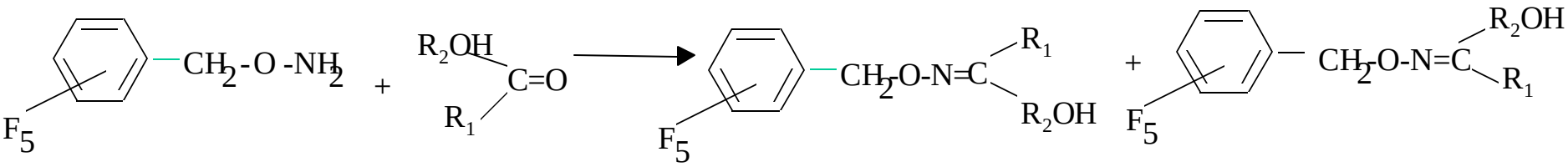
Hydroxyacetone (42%)

Methylglyoxal
+ Formaldehyde (8%)

OH·

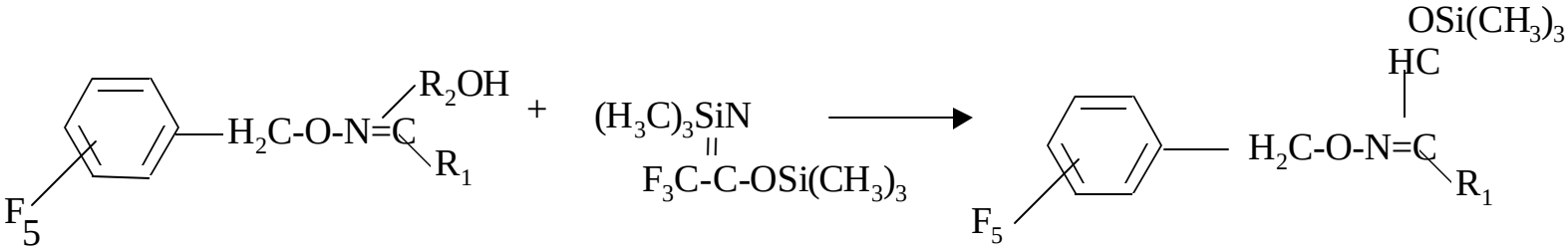
Methylglyoxal
(91%)

Scheme 1: Derivatization of a Hydroxy Carbonyl with *0*-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine (PFBHA)



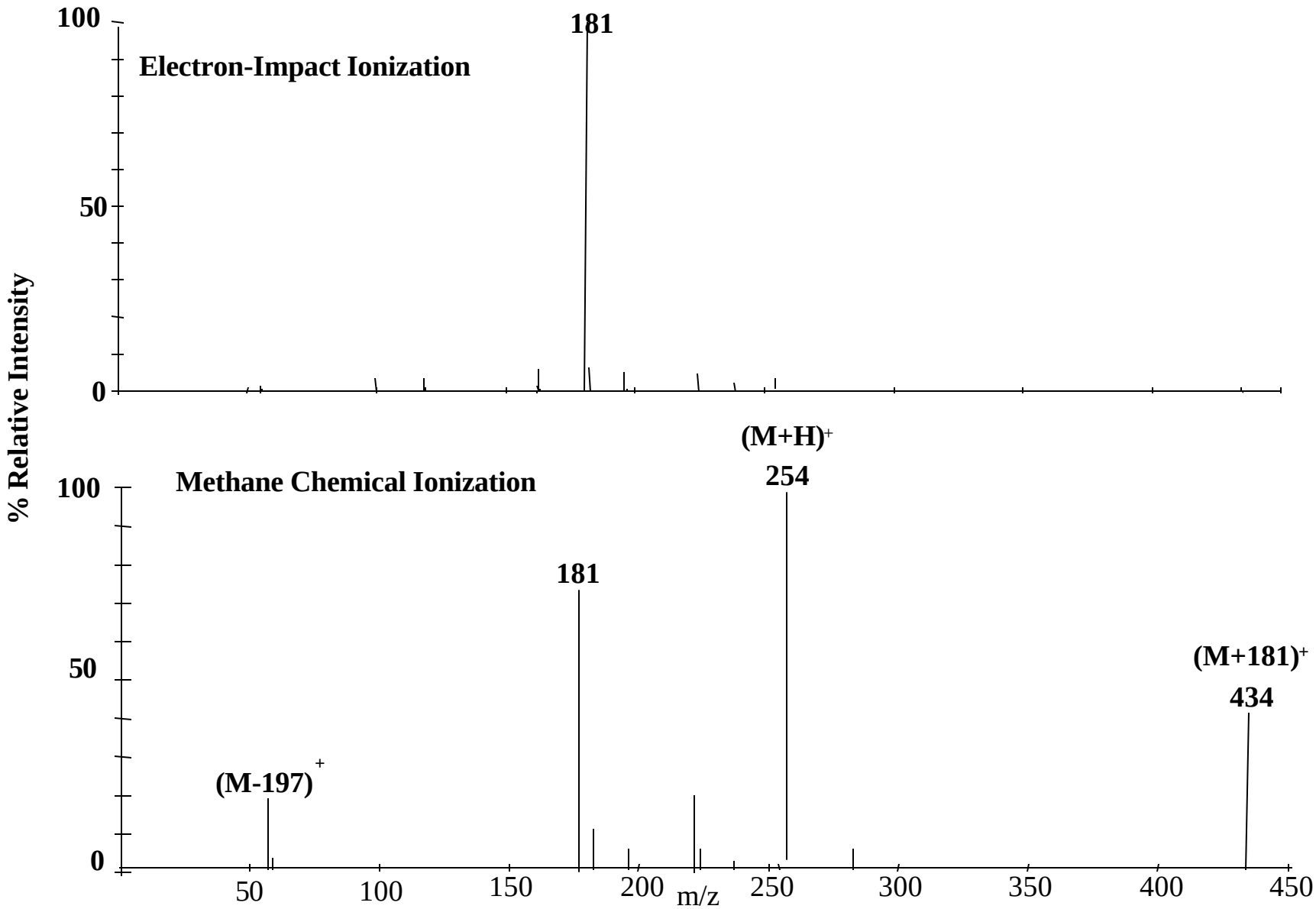
PFBHA A Hydroxy Carbonyl Hydroxy PFBHA Oxime Isomers

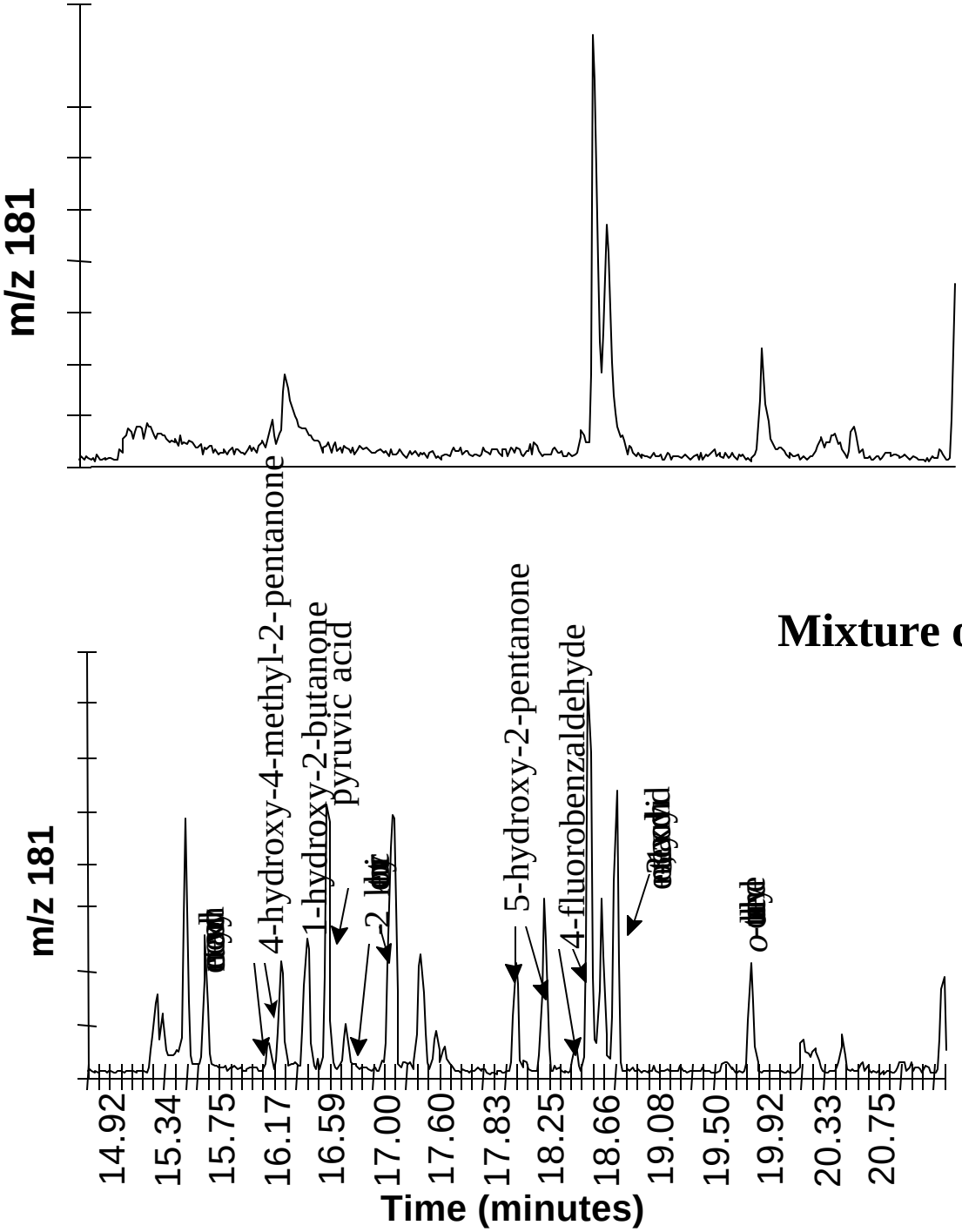
Scheme 2: Derivatization of a Hydroxy PFBHA Oxime with *bis* (trimethylsilyl) trifluoroacetamide (BSTFA)



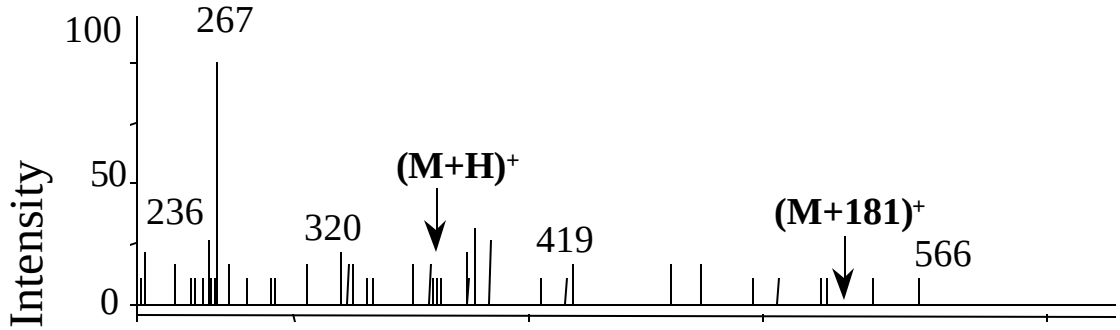
Hydroxy-PFBHA Oxime BSTFA PFBHA Oxime TMS Ether

Ion Trap Mass Spectra of the PFBHA Derivative of Propionaldehyde

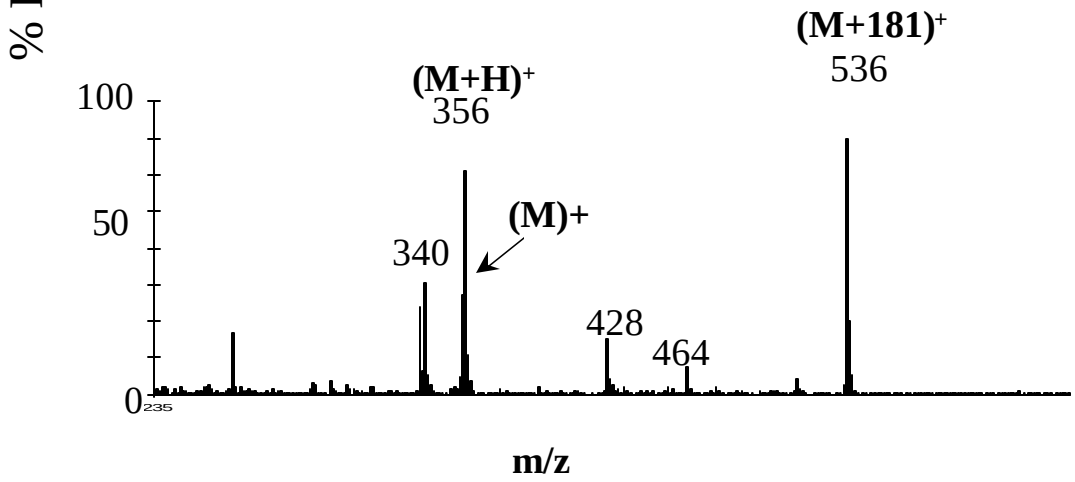



Mixture of PFBHA derivatives
m/z 181
Mixture of PFBHA/BSTFA derivatives
m/z 181
4-hydroxy-4-methyl-2-pentanone
1-hydroxy-2-butanone
pyruvic acid
5-hydroxy-2-pentanone
4-fluorobenzaldehyde
14.92
15.34
15.75
16.17
16.59
17.00
17.60
17.83
18.25
18.66
19.08
19.50
19.92
20.33
20.75
Time (minutes)

PFB Derivative of Pyruvic Acid

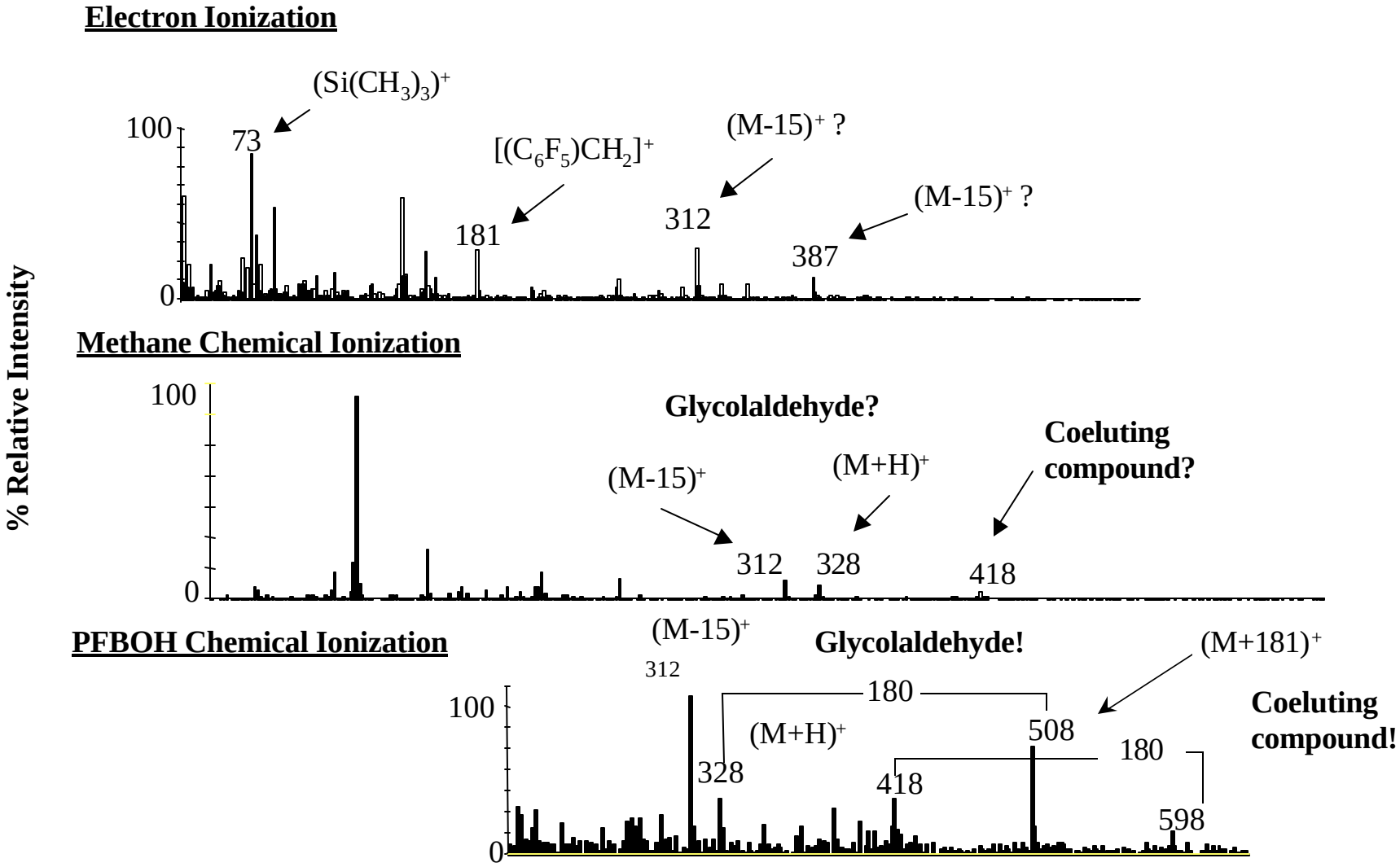


PFBHA/BSTFA Derivative of Pyruvic Acid



Sampling Air in Azusa, CA. as part of the 1997 Southern California Oxidant Study

Ion Trap Mass Spectra of a PFBHA/BSTFA Derivative in a Sample Extract of Air Sampled in Azusa, CA.



Novel Results of Study

1. First report of hydroxy acetone and 3-hydroxy-2-butanone in air.

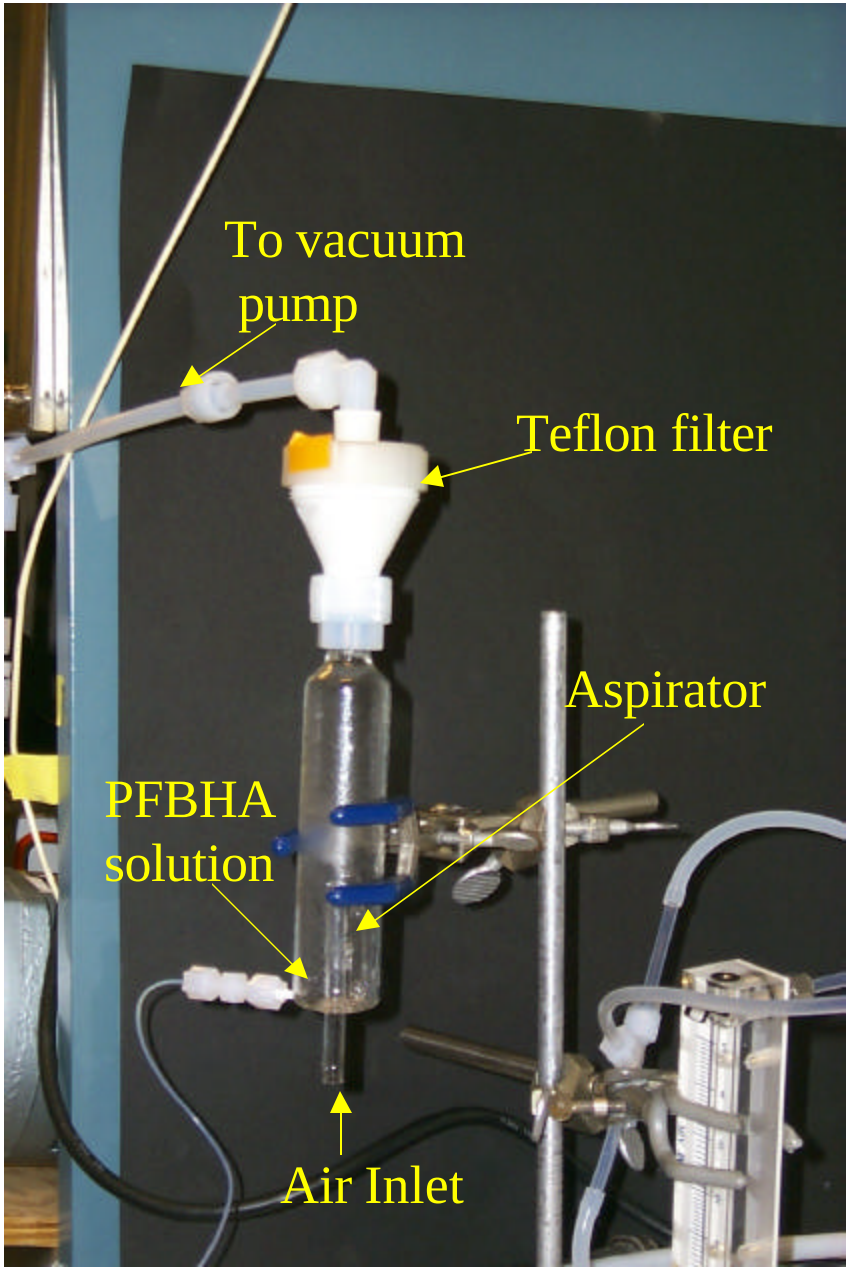
2. Demonstrates potential of method to measure water-soluble organics for which no or little ambient air data exists.

3. First study that applies pentafluorobenzyl derivatization along with ion trap mass spectrometry to field measurements.

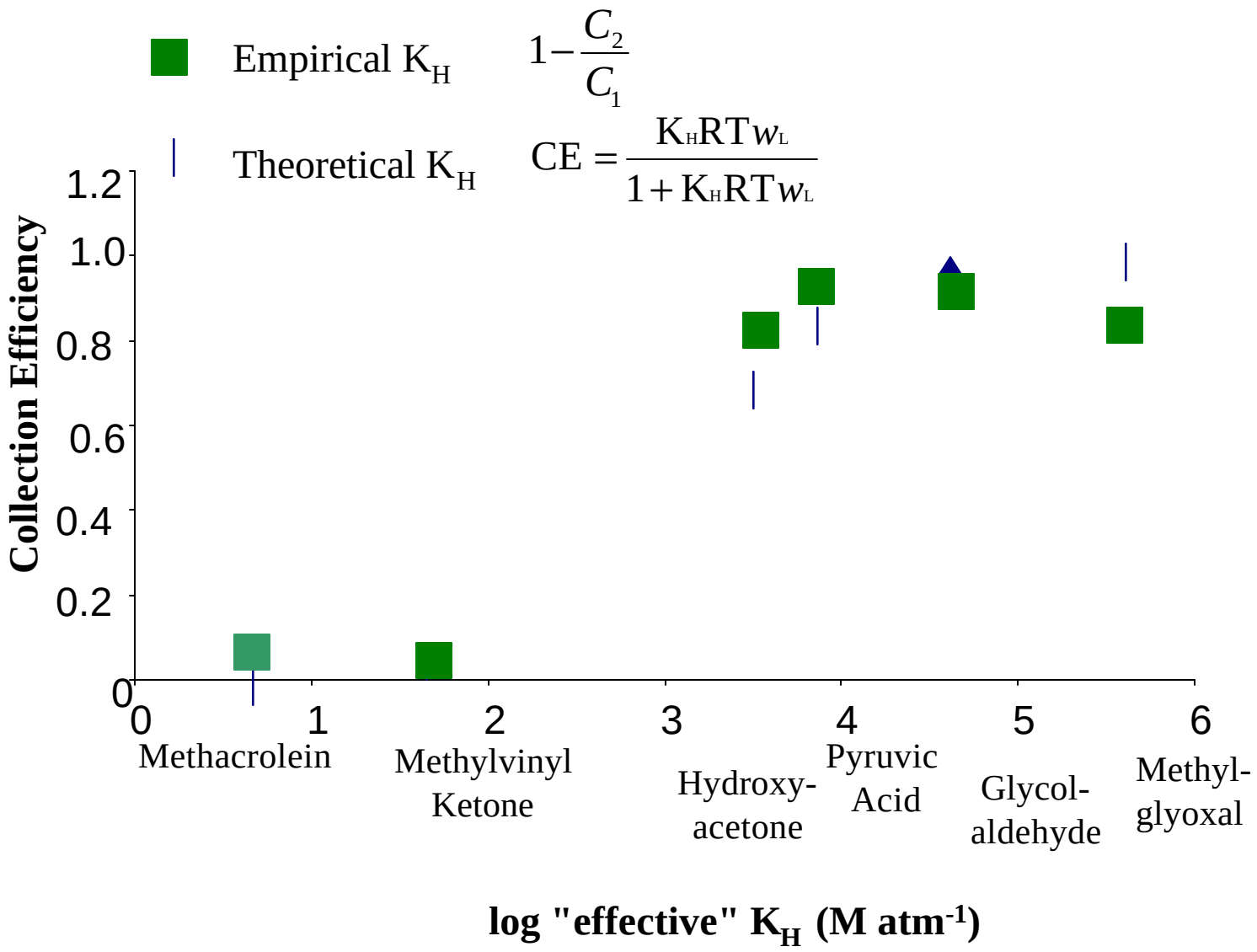
Spaulding et al., 1999. Anal. Chem. 71:3420:3427.

Sampling Methods

1. Impingers or solid sorbents
2. Coil scrubber with concurrent gas and liquid flows
3. Mist Chamber

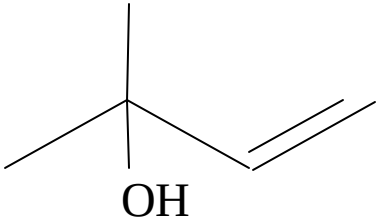

To vacuum pump
Teflon filter
Aspirator
PFBHA solution
Air Inlet

Relationship Beteween Collection Efficiency and log "effective" Henry's law Constants



The Blodgett Forest

2-methyl-3-buten-2-ol (MBO)



OH·

Acetone + Glycolaldehyde(50-60%)

Formaldehyde +
2-hydroxy-2-methylpropanal (30-35%)

OH·

Methylglyoxal
(12-22%)

Formaldehyde
(8-24%)

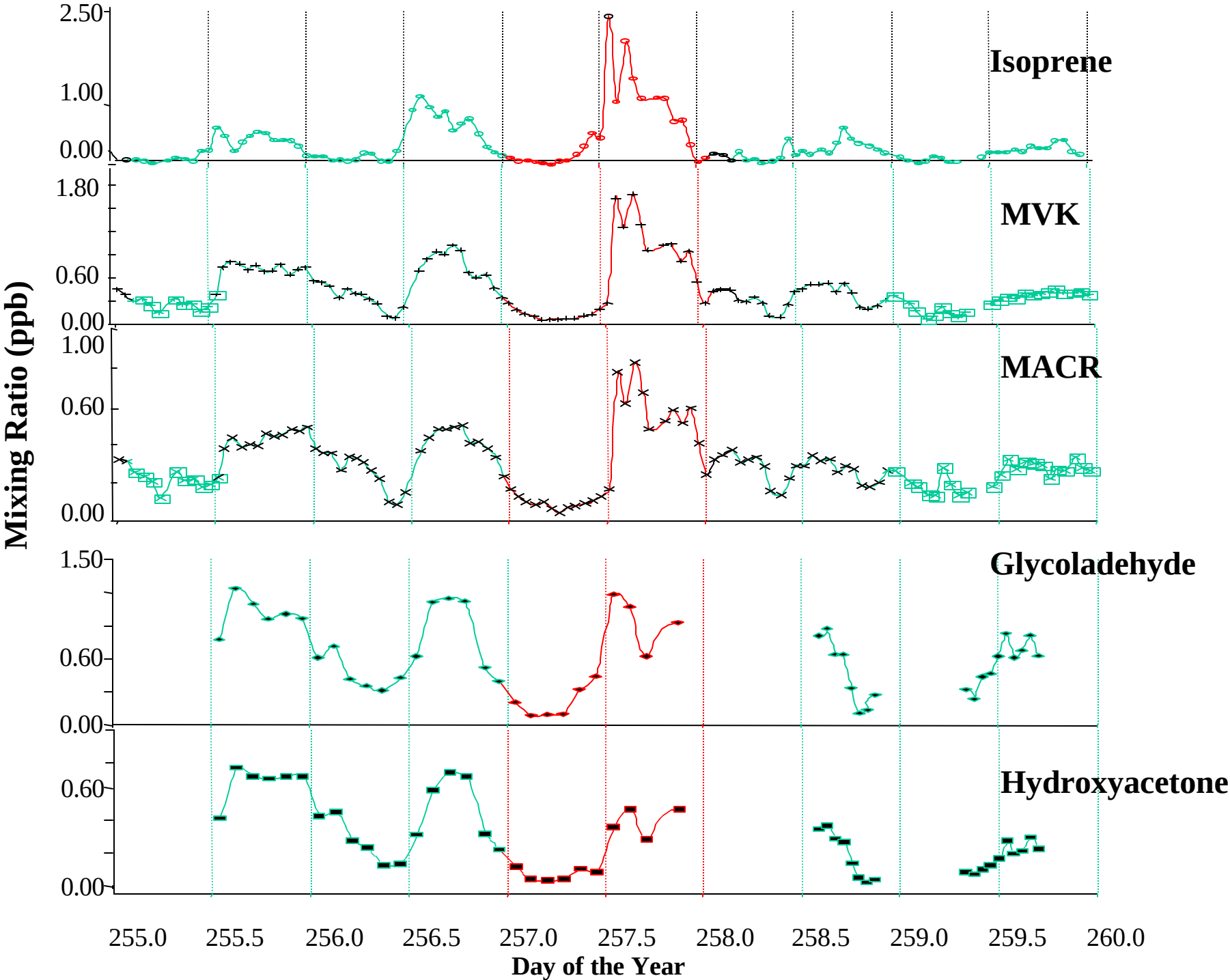
OH·

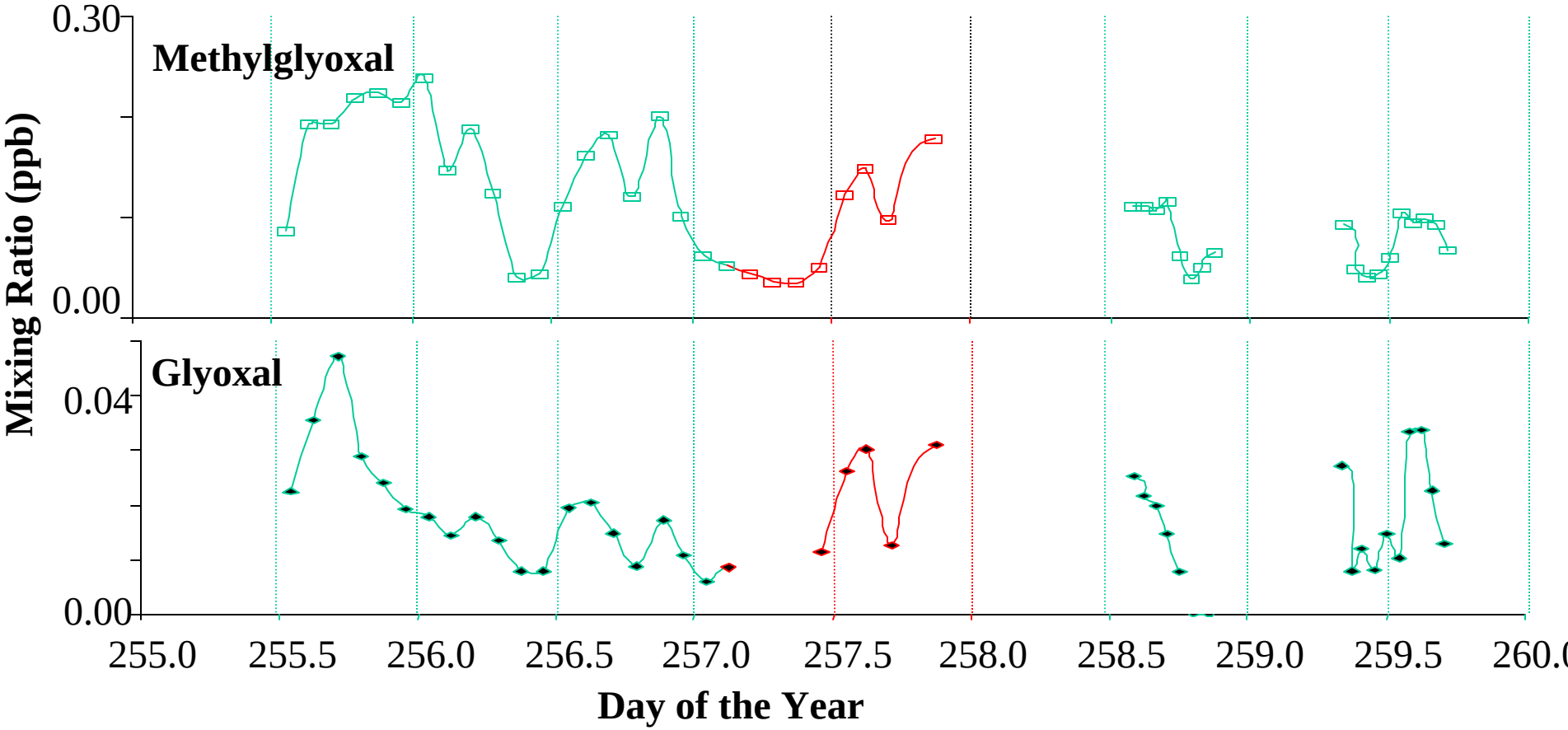
Glyoxal
(20%)

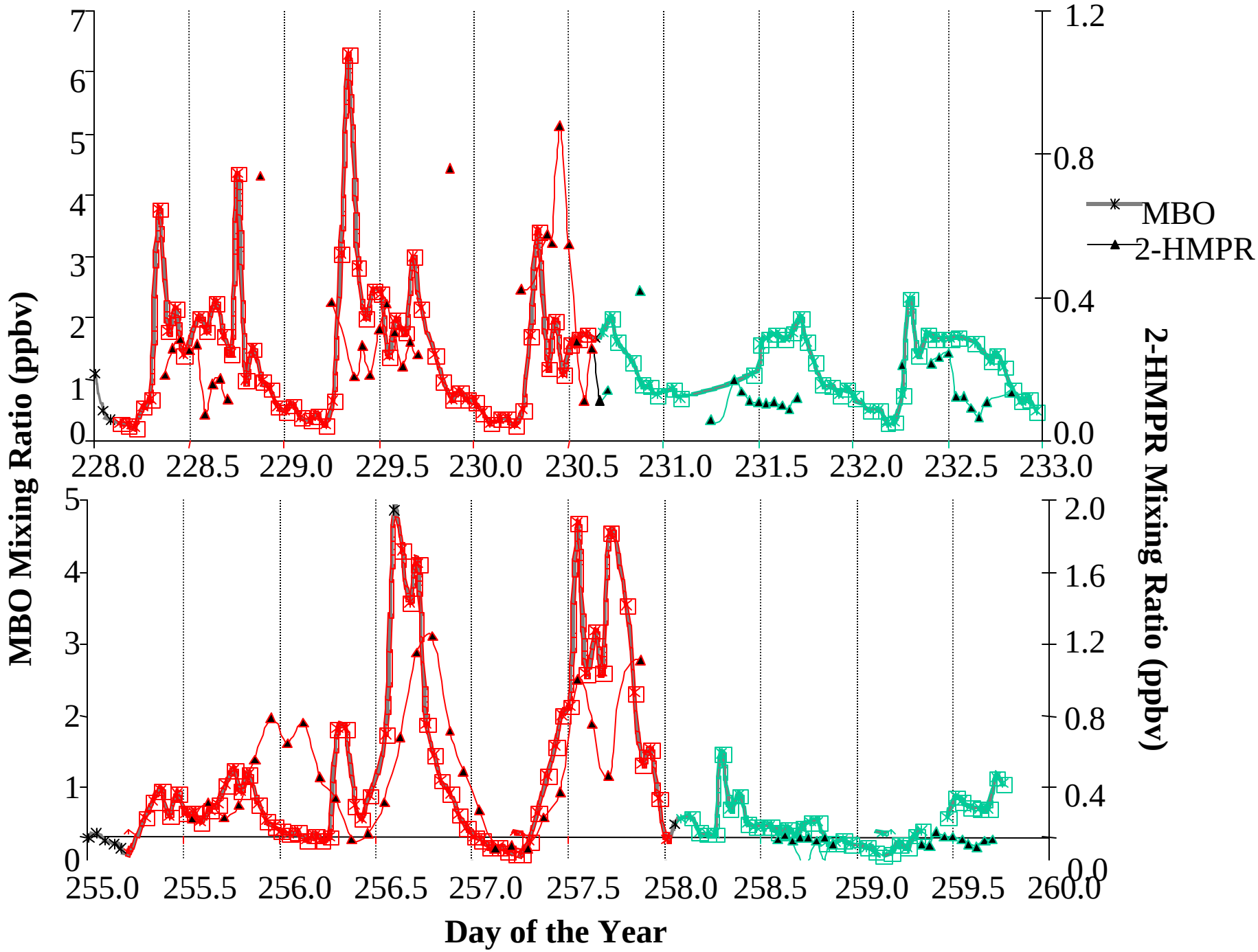
Formaldehyde
(80%)

Analyte	% Collection Efficiency	Limit of Detection (sampling time; min.) (ppt)	
		This study	Literature values
Glycolaldehyde	94±5	48 (10)	20 (20) 67 (180-240)
Hydroxy acetone	86±5	15 (10)	200 (180-240) 400 (15)
Glyoxal	86±20	2.7 (10)	20 (20) 20 (60-120)
Methyl glyoxal	83±20	7.7 (10)	20 (20) 50 (60-120)

Analyte	% Collection Efficiency	Limit of Detection (ppt) Range	Median
Glycoladehyde	92±15	15-52	31
Hydroxy acetone	92±12	1.7-32	20
2-Hydroxy-2-methyl-propanal (2-HMPR)	91±21	17-99	40
Glyoxal	91±21	2.8-11	7.2
Methyl glyoxal	84 ±11	2.5-11	5.2


Isoprene
MVK
MACR
Glycoladehyde
Hydroxyacetone
Mixing Ratio (ppb)
Day of the Year
2.50
1.00
0.00
1.80
0.60
0.00
1.00
0.60
0.00
1.50
0.60
0.00
0.60
0.00
255.0
255.5
256.0
256.5
257.0
257.5
258.0
258.5
259.0
259.5
260.0


Methylglyoxal
Glyoxal
Mixing Ratio (ppb)
0.30
0.00
0.04
0.00
255.0
255.5
256.0
256.5
257.0
257.5
258.0
258.5
259.0
259.5
260.0
Day of the Year


MBO
2-HMPR
MBO Mixing Ratio (ppbv)
2-HMPR Mixing Ratio (ppbv)
Day of the Year
0
1
2
3
4
5
6
7
0.0
0.4
0.8
1.2
228.0
228.5
229.0
229.5
230.0
230.5
231.0
231.5
232.0
232.5
233.0
0
1
2
3
4
5
0.0
0.4
0.8
1.2
1.6
2.0
255.0
255.5
256.0
256.5
257.0
257.5
258.0
258.5
259.0
259.5
260.0

Source Apportionment Methods: Biogenic vs. Anthropogenic Sources

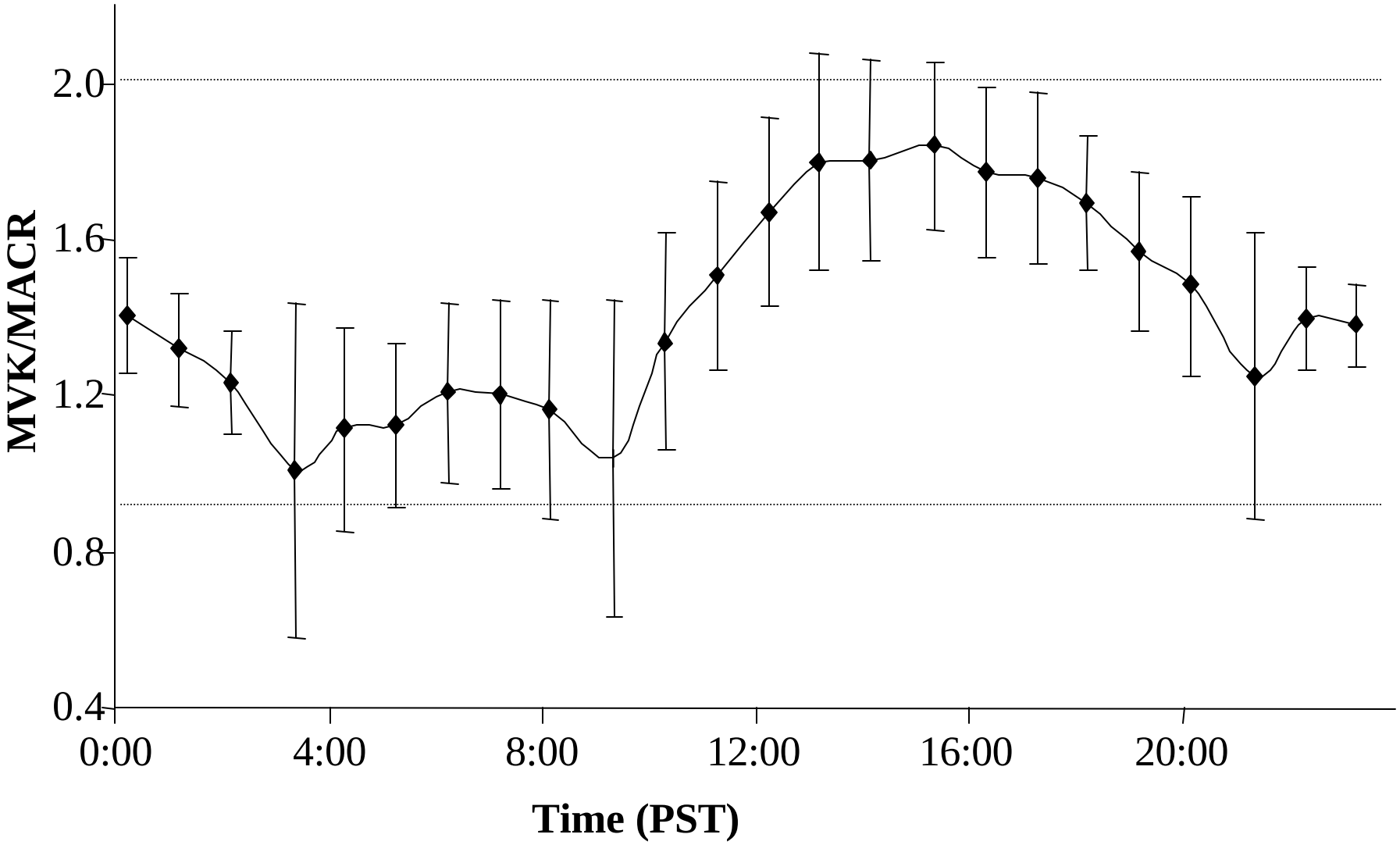
1. Compare predicted vs. measured ratios of products.

2. Factor analysis: groups variables whose data show simultaneous and consistent variation (e.g., analyzing many regression equations at once)

3. Regression analysis to correlate products to precursors.

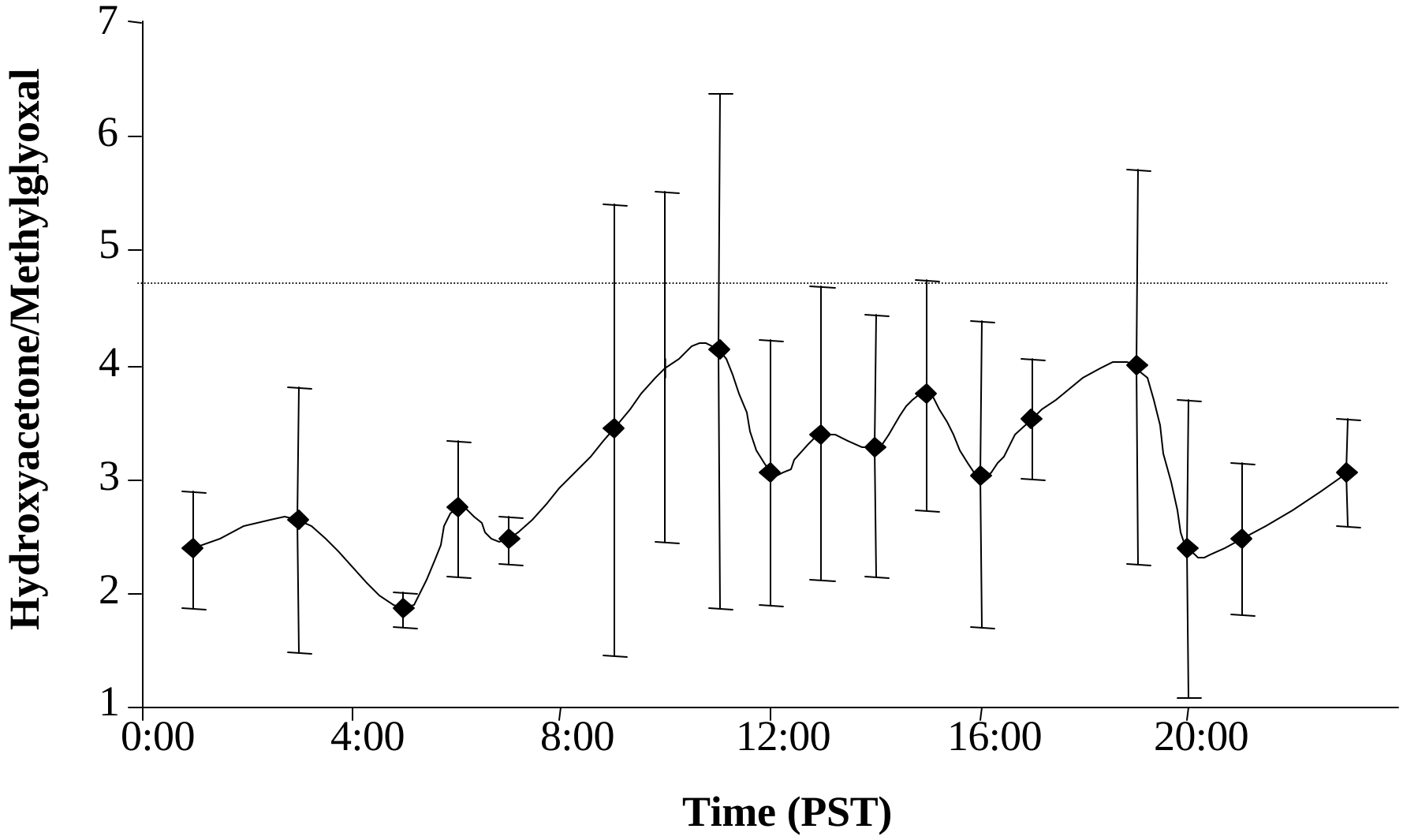
4. Analysis of anthropogenic precursors.

5. Compare predicted vs. measured ratios using kinetic box model.



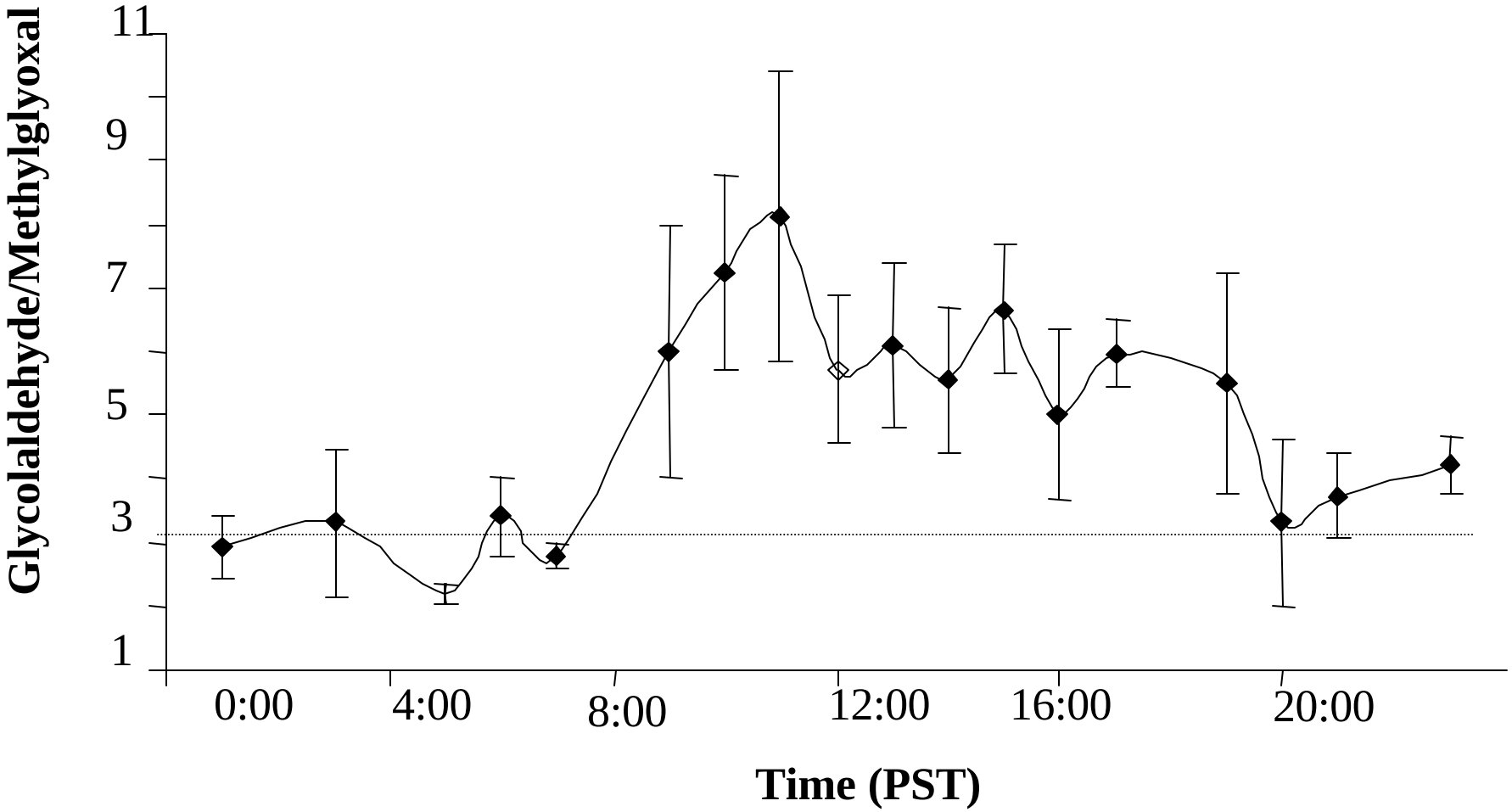
***Predicted MVK/MACR =1.0 at night and 2.0 during day, assuming isoprene is sole source.**

Measured values>Predicted values indicates other sources of hydroxyacetone.
Measured values<Predicted values indicates other sources of methylgloxal (MEG)



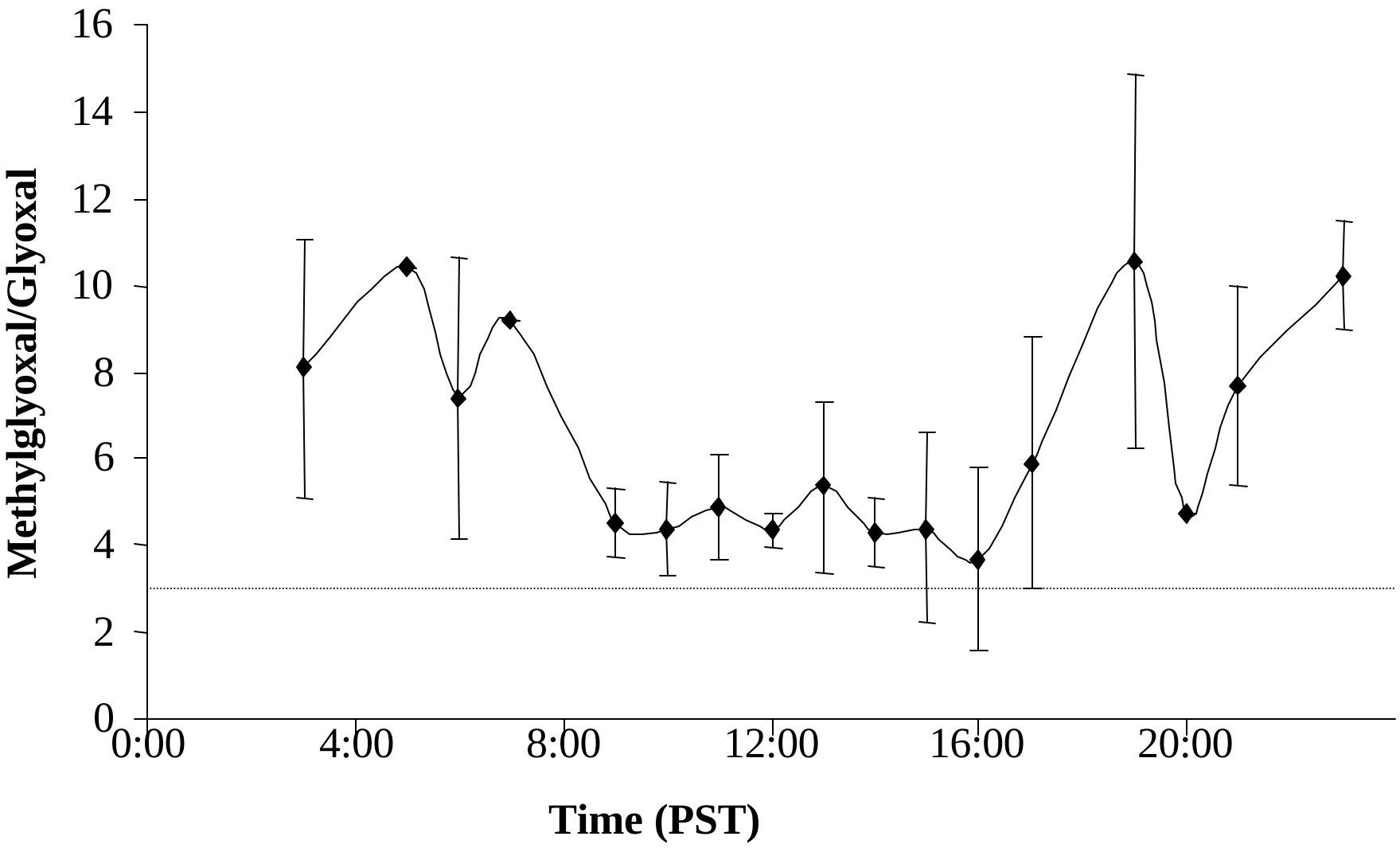
***Predicted hydroxyacetone/MEG=4.8, assuming isoprene is sole source, steady-state conditions and no losses from depostion.**

Measured values>Predicted values indicates other sources of glycolaldehyde.
Measured values<Predicted values indicates other sources of methylgloxal (MEG)



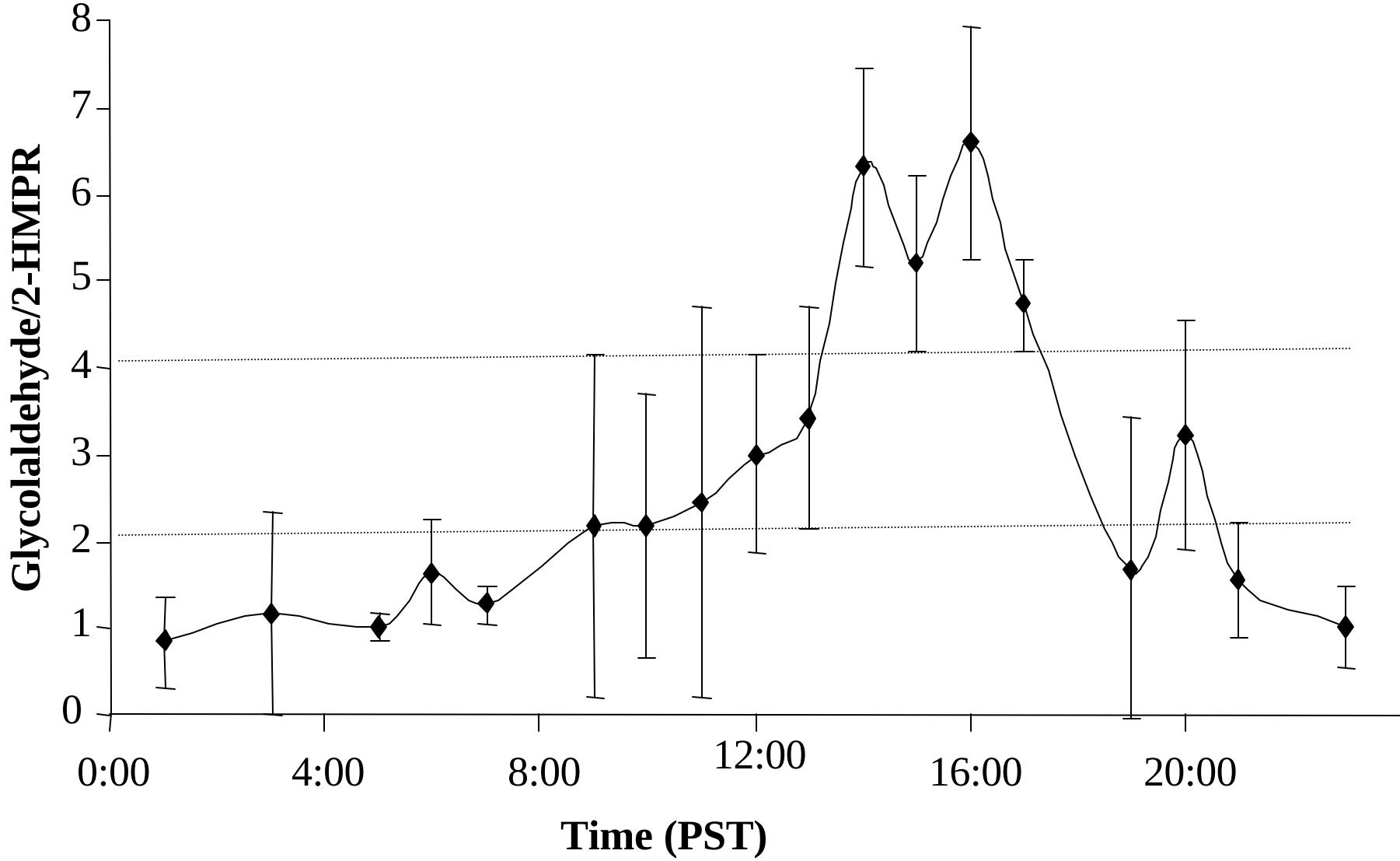
***Predicted glycolaldehdye/MEG=3.0, assuming isoprene is sole source, steady-state conditions and no losses from depostion.**

Measured values>Predicted values indicates other sources of methylglyoxal (MEG)
Measured values<Predicted values indicates other sources of gloxal (GLY)



***Predicted MEG/GLY=3.0, assuming isoprene is sole source, steady-state conditions and no losses from depostion.**

Measured values>Predicted values indicates other sources of glycolaldehyde
Measured values<Predicted values indicates other sources of 2-hydroxy-2-methypropanal (2-HMPR)



***Predicted GLY/2-HMPR=2.1-4.0, assuming MBO is sole source, high NOx conditions. steady-state conditions, and no losses due to depostion.**

Summary

1. Isoprene likely sole source of methacrolein and methylvinylketone.

2. High GLY/MEG and GLY/2-HMPR during day suggest isoprene and MBO as sources of glycolaldehyde, and perhaps anthropogenic sources of glycolaldehyde.

3. Low GLY/2-HMPR in evening indicates different mechanism that produces 2-HMPR but less glycolaldehyde.

4. High MEG/GLY and low Hydroxyacetone/MEG indicates other sources of methyl glyoxal.

Compound	Factor 1	Factor 2	Factor 3	Factor 4
Isoprene	0.896			
MBO	0.682			
Methacrolein	0.794		0.365	
Methyl vinyl ketone	0.898		0.308	
Glycolaldehyde	0.389	**0.824**		
Hydroxyacetone		**0.815**	0.405	
Methylglyoxal			**0.904**	
Glyoxal	0.282	0.427	0.710	
2-HMPR				0.763

Factor 1 = biogenic emissions and photooxidation products (isoprene, MBO, MVK, MACR, CO)
Factor 2= anthropogenic photooxidation products (glycolaldehyde, OH-Acetone, CO, glyoxal)
Factor 3= mixed origin/short lifetime (methyl glyoxal, glyoxal, CO, OH-Acetone)
Factor 4=uniquie biogenic oxidation products (2-HMPR)
Good correlation ≥ 0.6; weak correlation ≤ 0.4.

Source Apportionment for Photooxidation Products

Compound	% Relative Contribution to Measured Concentrations			
	Background	Biogenic	Anthropogenic	r^2
Hydroxy acetone	25	28	47	0.54
Glycolaldehyde	30	30	40	0.58
Methyl glyoxal	37	28	34	0.51
Glyoxal	63	13	24	0.38

Anthropogenic precursors

Reaction	Product Yields			
	Glycolaldehyde	OH-Acet.	Glyoxal	MeGly
Toluene + OH	minor	minor	0.08-0.15	0.08-0.25
Xylenes + OH	minor	minor	0.03-0,13	0.11-0.42
Trimethylbenzenes+OH	minor	minor	.05-0.08	0.15-0.64
Ethene+OH	-	-	-	-
Propene+OH	-	ND	-	ND
1,3-butediene + OH	ND	ND		ND

Comparison of measured product ratios vs. predicted ratios using a simple kinetic model.

Products	Predicted Product Ratios		Measured Product Ratios
	Model 1	Model 2	(Mean±S.D.)
MVK/MACR	1.8	3.1	1.8±0.3
Hydroxyacetone/GLY	0.52	0.89	0.59±0.12
Hydroxyacetone/MEG	2.5	4.0	3.3 ±1.2
MEG/GLY	4.2	2.0	4.3 ± 0.8
GLY/MEG	4.8	4.5	5.6±1.8
GLY/2-HMPR	3.9	7.0	6.3±1.6

Model 1: considers phtooxidatition of isoprene and MBO.
Model 2: considers photooxidation of anthropogenic and biogenic emissions.

Conclusions

1. Glycolaldehyde and hydroxy acetone strongly influences by anthropogenic sources, as determined by factor analysis, regression analysis, and comparison to kinetic model.

2. Low correlation of methyl glyoxal and glyoxal with CO and agreement of MEG/GLY with kinetic box model that only considered isoprene photochemistry suggest small anthropogenic influence.

.

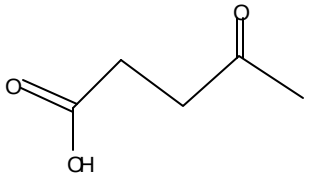
3. Low GLY/2-HMPR ratios suggests mechanism that produces 2-HMPR but less glycolaldehyde. Suggest studies that investigate effect of NO_X concentration on photooxidation of MBO.

4. More studies needed to investigate regional influences of photooxidation products.

Compounds Previously Unidentified in $PM_{2.5}$

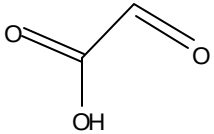
Light- and Heavy- Duty Bore

Levulinic Acid



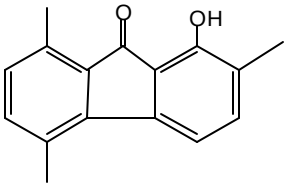
Light- Duty Bore

Glyoxylic Acid



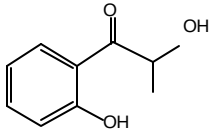
Heavy-Duty Bore

$C_{16}H_{14}O_2$ (1-hydroxy-2,5,8-trimethyl-H-fluoren-9-one)

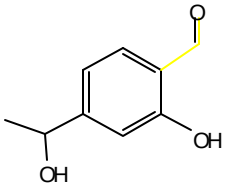


or

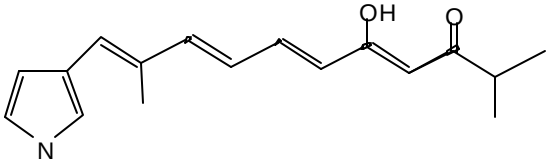
$C_9H_{10}O_3$ (2-hydroxy-5-(1-hydroxyethyl) benzaldehyde



(2-hydroxy-1-(4-hydroxyphenyl)1-propanone



$C_{17}H_{21}NO_2$ Wallemia A



Some Contributions of Pentafluorobenzyl Derivatization in Concert with GC/Ion Trap Mass Spectrometry to Atmospheric Chemistry

1. Measurement of novel oxidation products in chamber studies to elucidate chemical reaction mechanisms.

2. Ambient measurements of previously unidentified species

3. Measurements of novel organics in $PM_{2.5}$

Acknowledgements

Reggie Spaulding

Allen Goldstein, Gunnar Schade, University of California, Berkeley

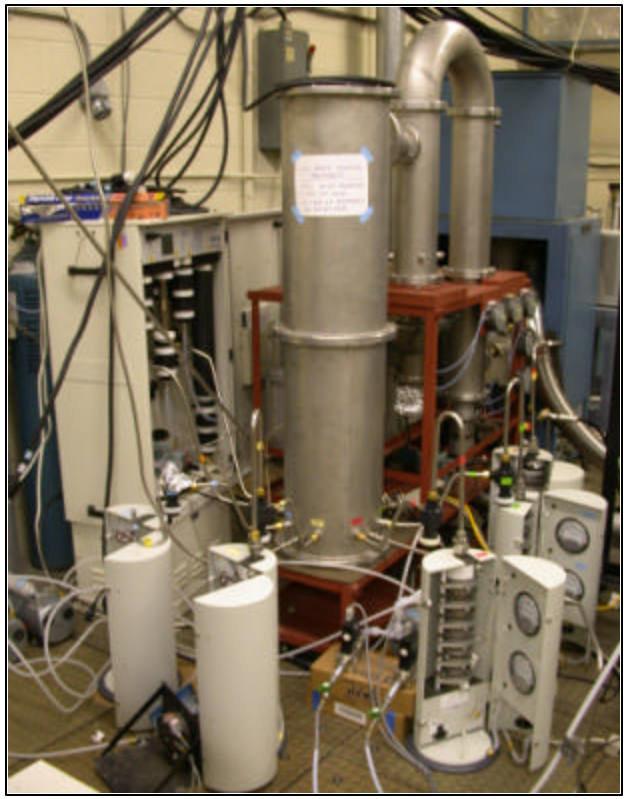
California Air Resources Board

National Science Foundation.

LDV on dynamometer

Tailpipe emission

UCD CEE dilution air system



Stack dilution tunnel and residence chamber

Denuder-filter-PUF sampling train

Oxygenated organics tentatively identified in a sample extract of emissions from a light-duty vehicle.

Carbonyls

	D_1	D_2	Filter	PUF
C_4-saturated aliphatic	X			
C_5-saturated aliphatic	X			
C_5-unsaturated aliphatic				X
C_6-unsaturated aliphatic	X	X		
Methylbenzaldehyde	X	X		
Ethyl-benzaldehyde	X			
Propyl-benzaldehyde	X			
Hexanedione	X	X		
Nonanedione	X	X		
Undecanedione	X	X		
Indanone	X			
Fluorenone	X			
Acenaphthenone	X	X		
Naphthoquinone	X	X		
C_5-aliphatic hydroxycarbonyl				X
C_6-aliphatic hydroxycarbonyl	X	X		
C_7-aliphatic hydroxycarbonyl	X	X		
Hydroxybenzaldehyde	X	X		
Hydroxymethylbenzaldehyde	X			

Carboxylic acids

	D_1	D_2	Filter	PUF
Acetic acid				X
Propionic acid			X	X
Hydroxypropionic acid				X
Hexanoic acid				X
Nonanoic acid	X	X		
Decanoic acid	X	X		
Tridecanoic acid	X	X		
Palmitic acid	X	X		
Stearic acid			X	
Nonadecanoic acid	X	X		
Benzoic acid	X	X		
Methylbenzoic acid	X	X		
C_3H_7-Naphthalenecarboxylic			X	

Phenols

Phenol	X	X		X
Methylphenol	X	X		
C_2H_5-phenol	X	X		
C_3H_7-phenol	X	X		
C_4H_9-phenol	X	X		
Naphthol	X			
Hydroxyacenaphthylene			X	