Total Non-Methane Organic Carbon

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Motivation

- *Goals: 1. Measure total non-methane organic compounds (TNMOC), and*
- *2. Determine the relationship between TNMOC and the sum of the speciated volatile organic compounds (VOC's) measured by standard techniques (Gas chromatograph/ flame ionization detector).*
- VOC's are one of the key determinants of air quality and control strategies.
- Standard measurement methods are known to detect hydrocarbons and their oxidation products incompletely.

Possible Types of Excess TNMOC Compared to the Sum of Speciated VOC's
(Standard VOC Measurement)

- Compounds that are lost in the inlet or column (polars, semi-volatiles).
- Compounds that are obscured in the GC baseline (hydrocarbons).
- Heteroatom compounds that have a reduced response in an FID.

Possible Sources of Excess TNMOC Compared to the Sum of Speciated VOC's in Ambient Air

- Photochemical oxidation of hydrocarbons.
- Direct source emissions. These may be either oxygenates or semi-volatile hydrocarbons.

Method

- Trap VOC's from 2 ambient air samples simultaneously in a cryogenically cooled trap. Allow CO, CO_2, and CH_4 to pass through.
- Desorb both VOC samples.

Speciated VOC's: analyze directly with DB-1 Column, GC/FID. = Standard Measurement

TNMOC: oxidize CO_2, analyze as methane w/ GC/FID. = Total VOC's

3. Compare TNMOC with the standard measurement of VOC's.


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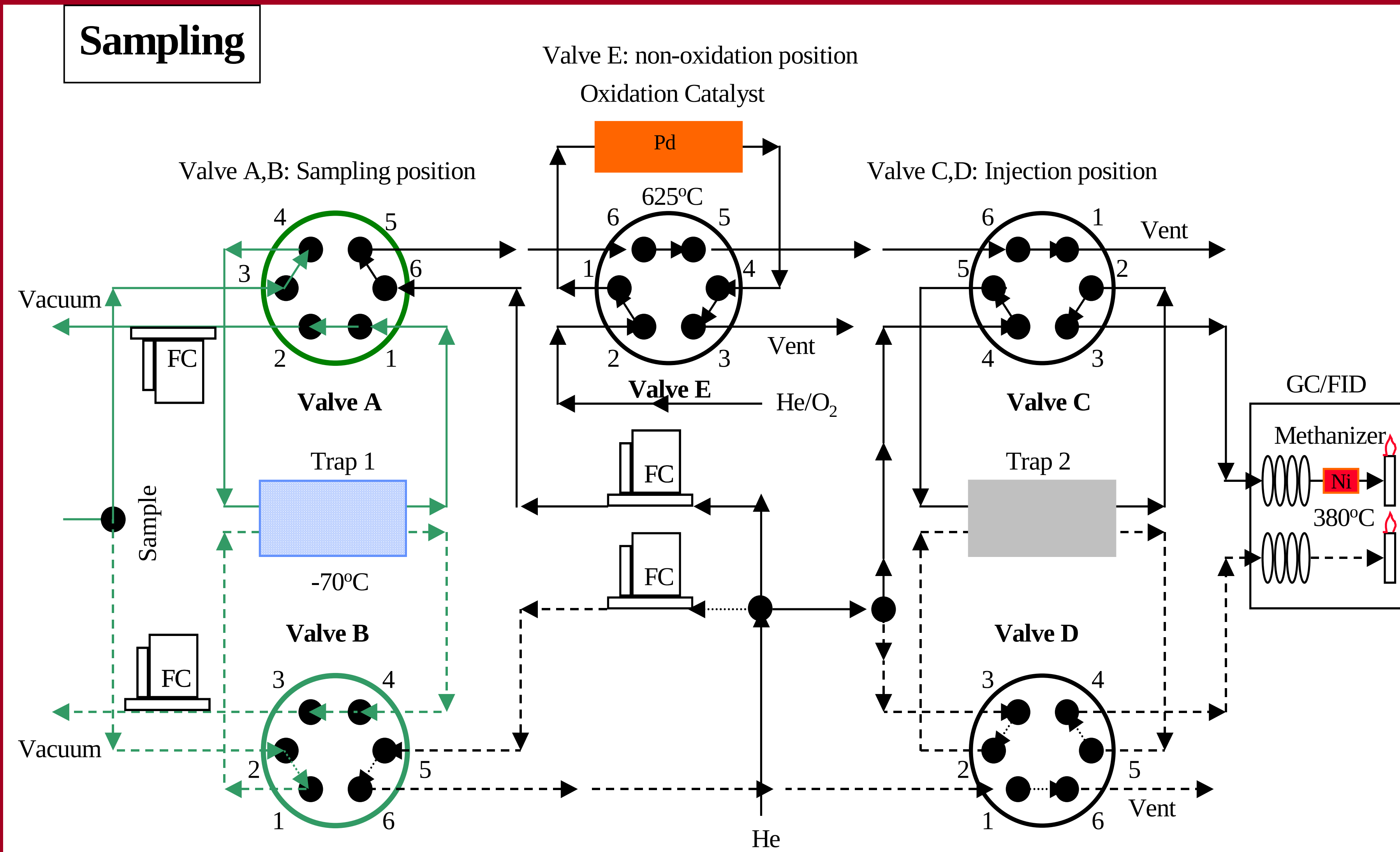
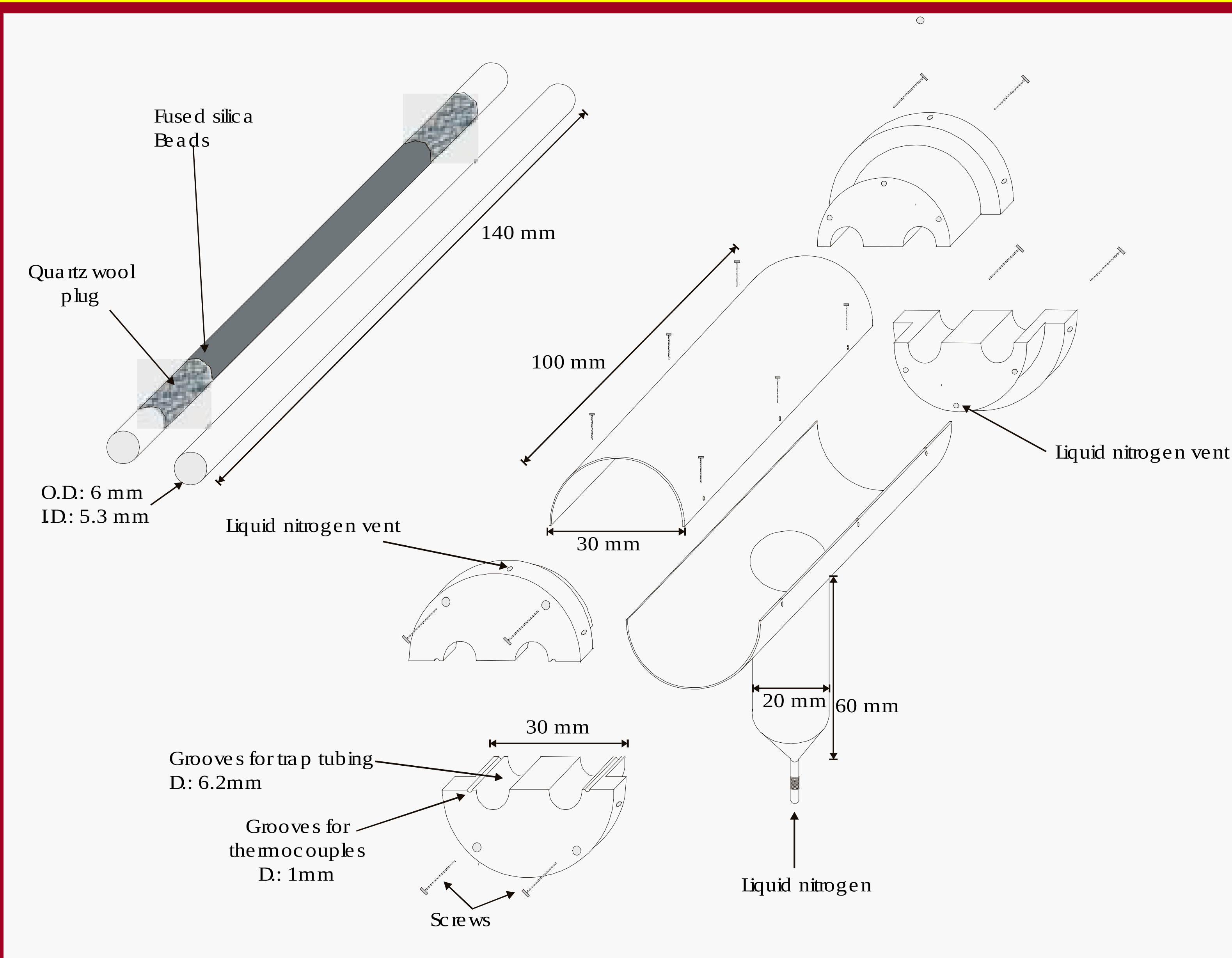
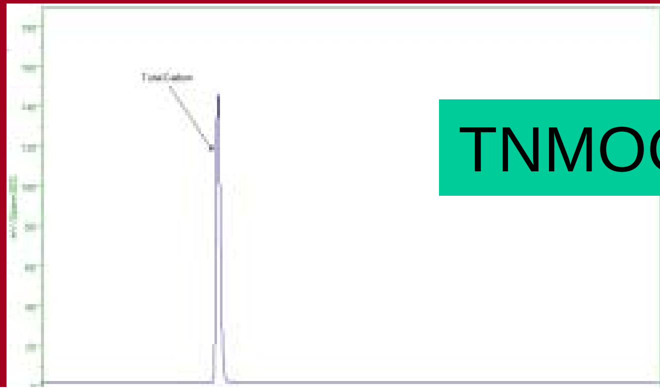
Flow Schematic

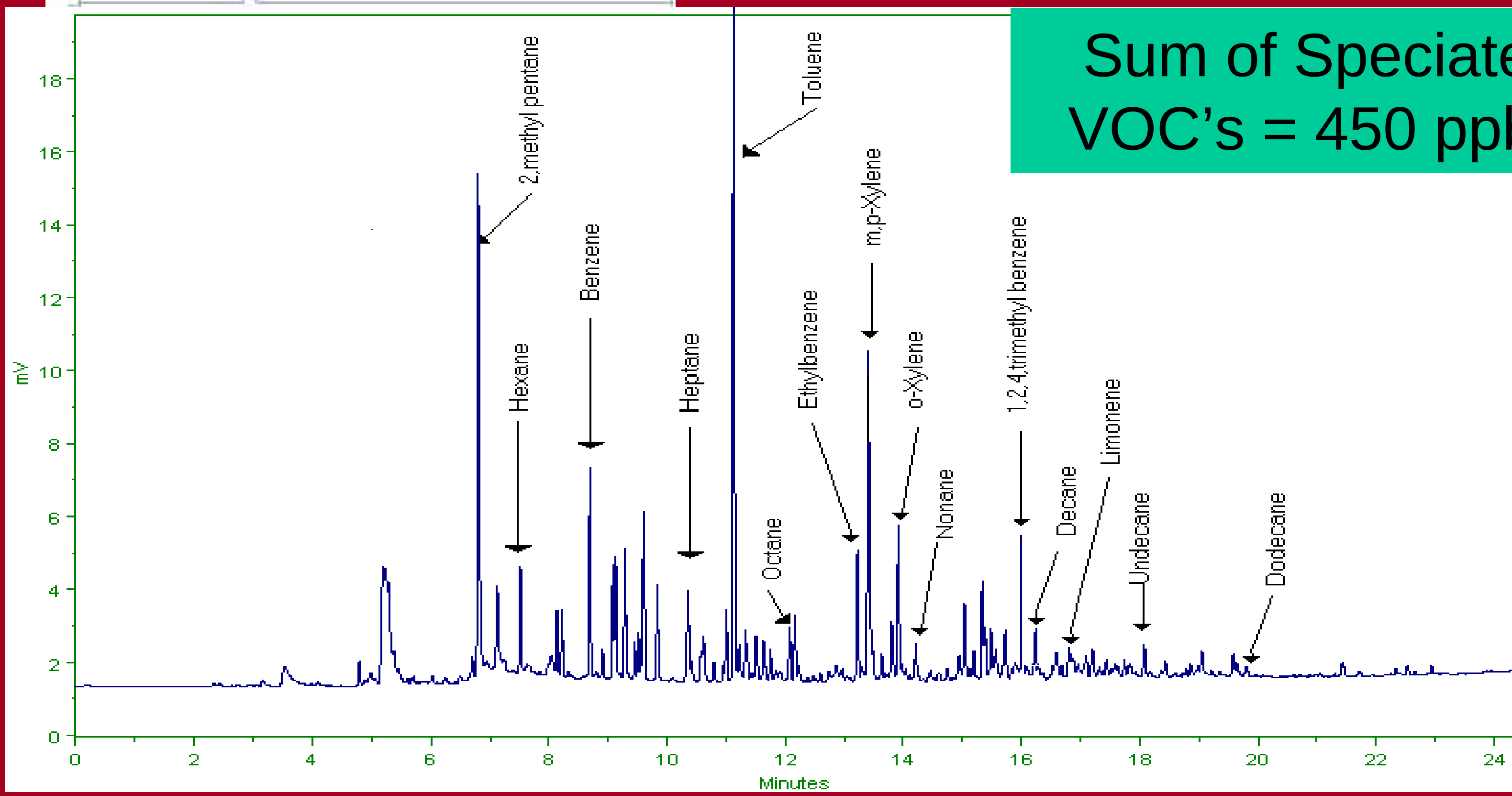


Trap I Design



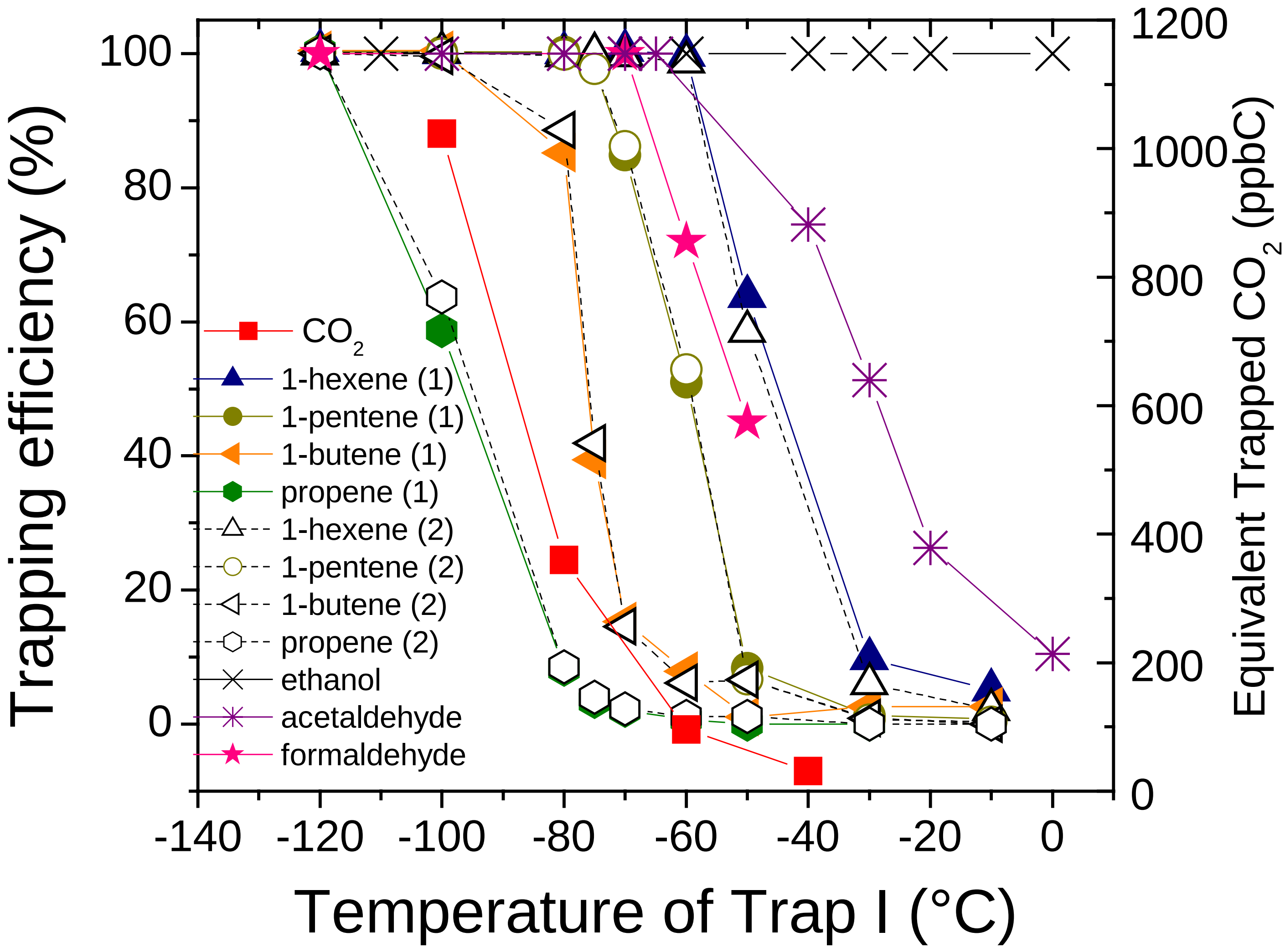


TNMOC = 620 ppbC



Sum of Speciated VOC's = 450 ppbC

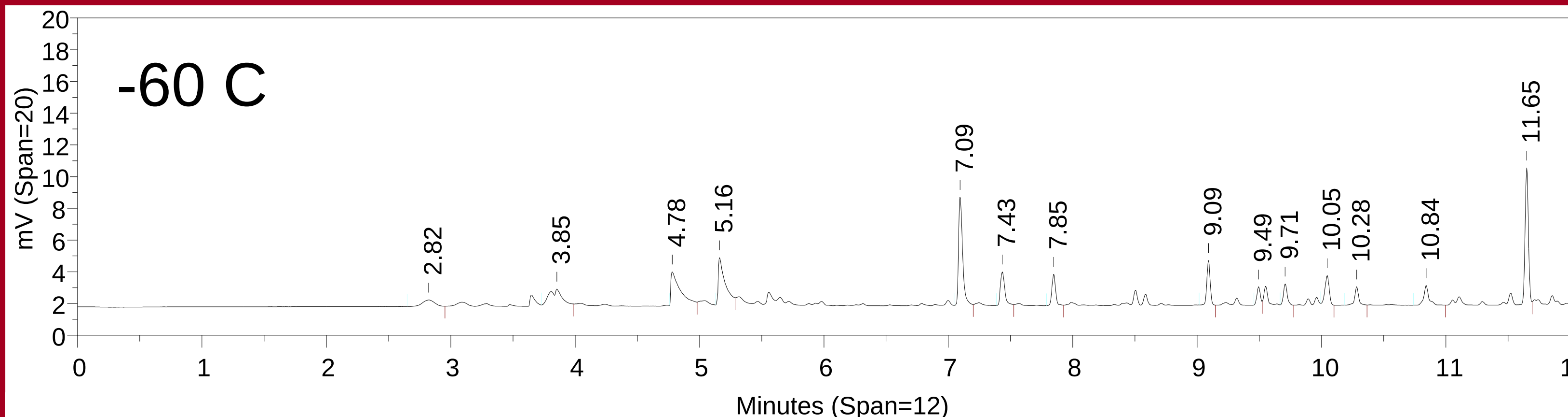
Trapping Efficiency vs. Temperature

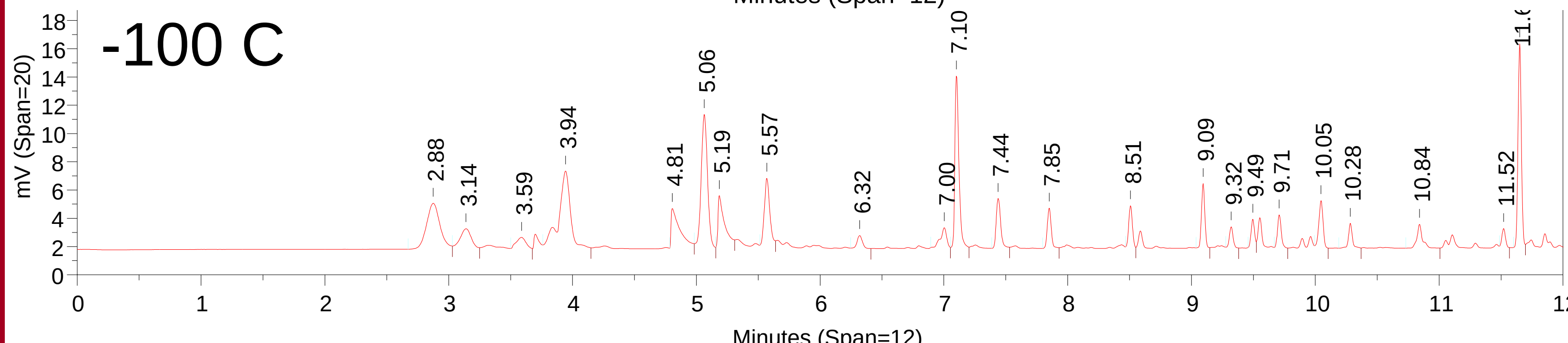


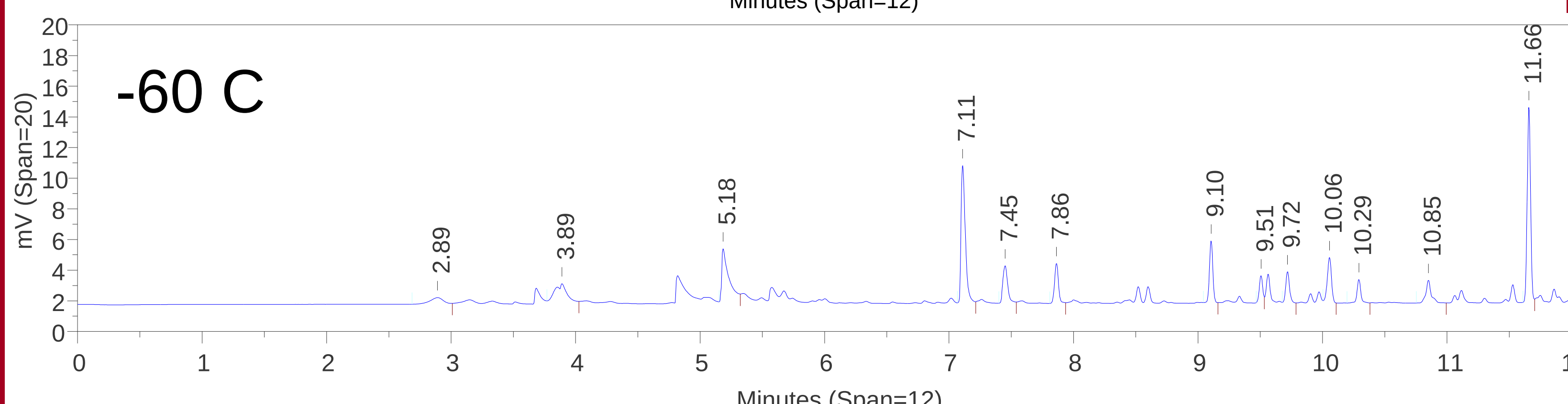
Correction for Light Hydrocarbons

- Hydrocarbons with 4 or 5 carbon atoms trap with efficiencies between 5 and 80% and C_2 and C_3 hydrocarbons only minimally. Acetaldehyde, methanol, ethanol and acetone etc. also elute in this region, and are collected at 100%.
- Loss of C_3 - C_5 hydrocarbons was corrected as follows:
- 20 samples were trapped at –100 °C where 100% of C_4 and C_5's trap and 64% of C_3's trap. These were compared to the chromatograms collected at –60 °C immediately before and after.

Light Hydrocarbons







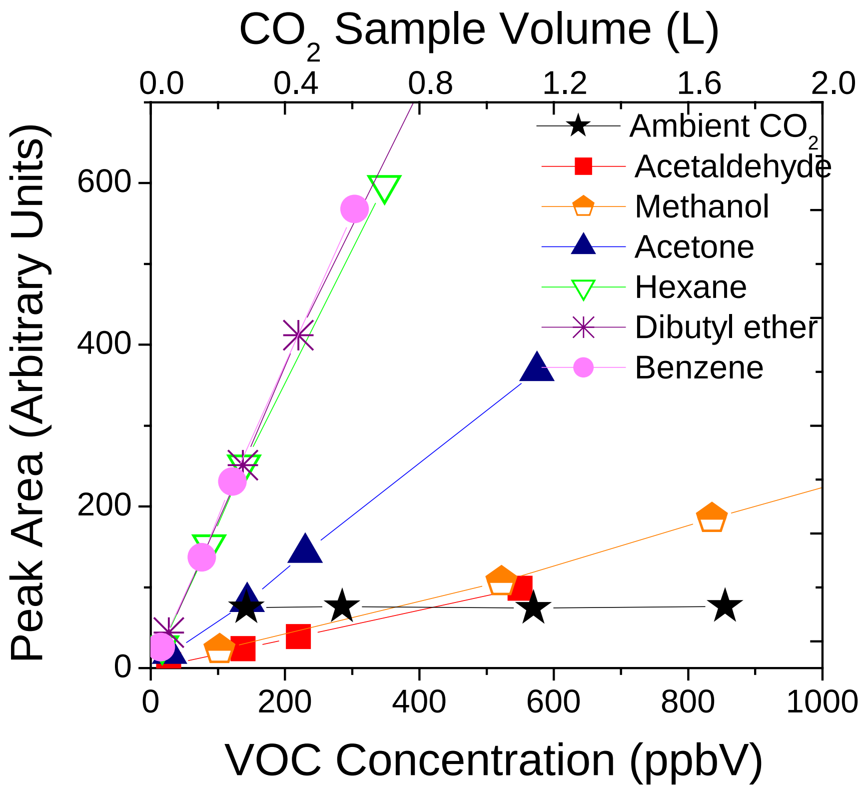
Correction for Light Hydrocarbons

- C_3 concentrations were corrected using their trapping efficiencies.
- Peaks eluting between C_3 and C_5 were normalized to the sum of spec. VOC's at –100 °C.
- The result was compared to the –60 °C chromatograms, also normalized.
- The difference, equal to the lost C_3-C_5 hydrocarbons at –60 °C, averaged 12.5% of the sum of speciated VOC's at –60 °C.
- 6.5% was added to account for untrapped C_2's, based on SCOS-97 Azusa data (McCauley, 1999).

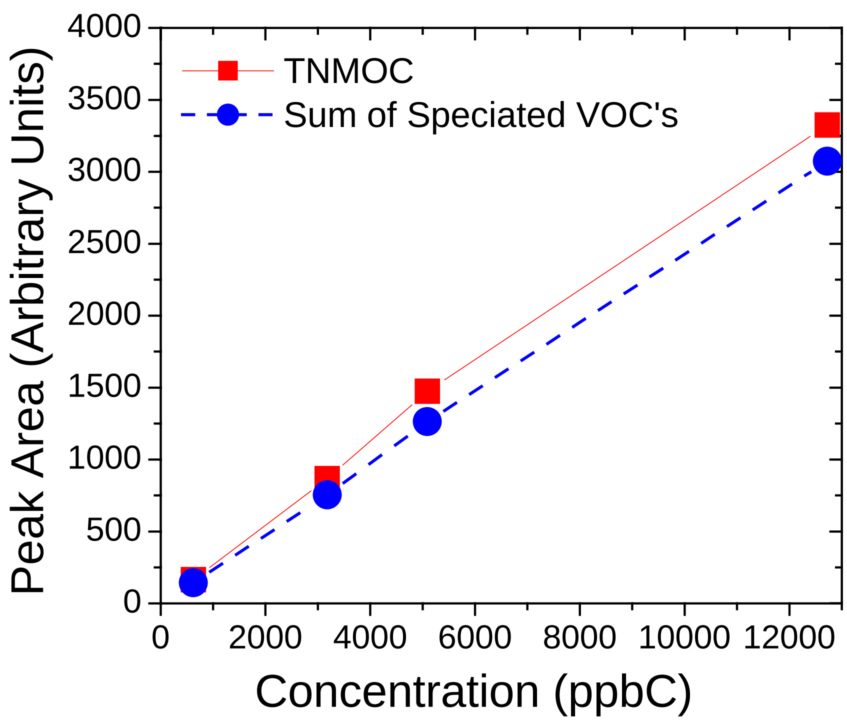
Correction for Light Hydrocarbons

- Because the lost light hydrocarbons are added to both the TNMOC and the Sum of Speciated VOC's, they have a minor effect on the ratio of the two:
- This correction shifts the average TNMOC/sum of speciated VOC’s ratio from 1.37, 1.77 and 1.1 to 1.30, 1.65 and 1.1 for UCLA 2000 summer clear, cloudy, and winter.
- A similar peak-by-peak correction for the Azusa data shifted the that average ratio from 1.29 to 1.25.

Linearity

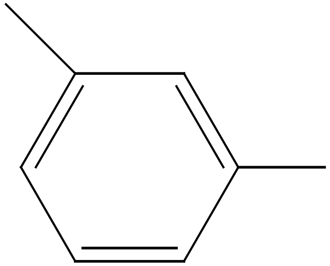


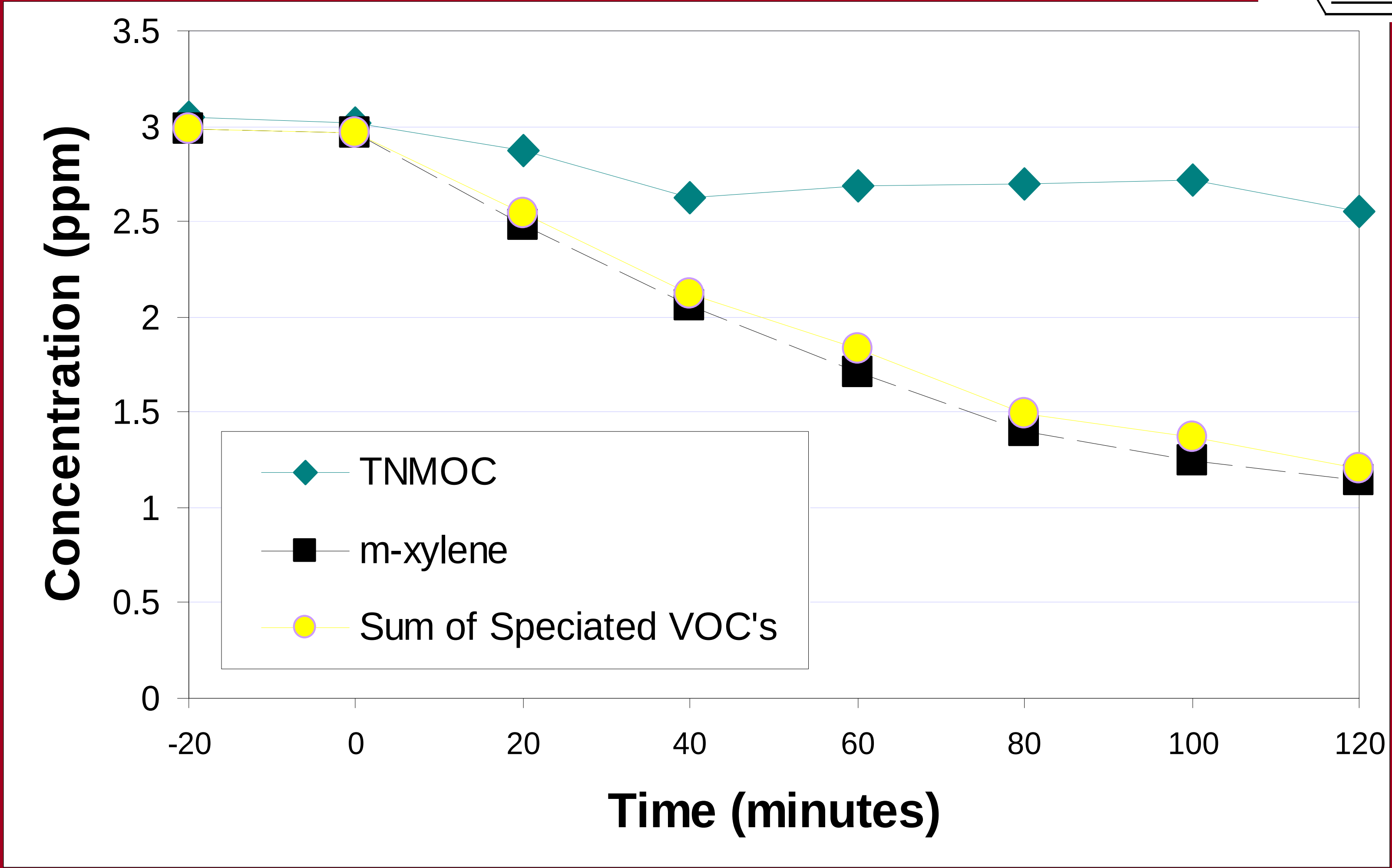
CO2 Sample Volume (L)
0.0
0.4
0.8
1.2
1.6
2.0
Ambient CO2
Acetaldehyde
Methanol
Acetone
Hexane
Dibutyl ether
Benzene
Peak Area (Arbitrary Units)
0
200
400
600
0
200
400
600
800
1000
VOC Concentration (ppbV)



TNMOC
Sum of Speciated VOC's
Peak Area (Arbitrary Units)
0
500
1000
1500
2000
2500
3000
3500
4000
0
2000
4000
6000
8000
10000
12000
Concentration (ppbC)

Chamber Oxidation of m-Xylene





Oxidation products of this aromatic are not measured by standard GC/FID, but are measured well with the TNMOC channel.

AQMD Intercomparison

TNMOC Instrument			SCAQMD PAMS GC	
Sampling Times (PST)	TNMOC (ppmC)	TNMOC corrected for light hydrocarbons	Sampling Times (PST)	Total Speciated VOC’s (ppmC)
10:00 - 11:00	1.4			
11:30 - 12:30	1.7		9:00-12:00	1.53
Average	1.55	1.7		
11:30 - 12:30*	0.5			
13:00 - 14:00	0.9		11:00-14:00	0.63
Average	0.7	0.75		
14:30 - 15:30*	1.8			
16:00 - 17:00	5.2		14:00-17:00	3.22
Average	3.5	3.8		

Trapped Ambient CO_2

Period	Sample Volume (mL)	n	$[CO_2]$* Average ± SD (ppbC)	$[CO_2]$ min. (ppbC)	$[CO_2]$ max. (ppbC)	[TC] Average ±SD (ppbC)	[TC] min. (ppbC)	[TC] max. (ppbC)
Sunny 09/12/00-10/09/00	1140	15	49±14	36	86	329±178	91	835
	570	5	129±8	121	142			
Cloudy 09/12/00-10/09/00	1140	10	54±8	41	64	205±120	68	620
	570	8	115±13	84	126			
11/30/00-12/20/00	1140	11	59±5	50	69	269±172	35	889
	570	2	126±16	115	137			

Detection Limits and Uncertainties

Data Type	Detection Limit	Uncertainty
TNMOC channel	35 ppbC	±10 –20 ppbC; ± 8% at concentrations over 200 ppbC, increasing below
Sum of Speciated VOC's Channel	1 ppbC	+ 3-5% - 10-30%
Individual VOC's	10 pptC	± 3-20%, depending on separation
TNMOC/Sum of Speciated VOC's Ratio	__	± 0.05 to ± 0.10 for ratios between 1 and 2, depending on concentration, - 0.1, + 0.5 for ratios above 2

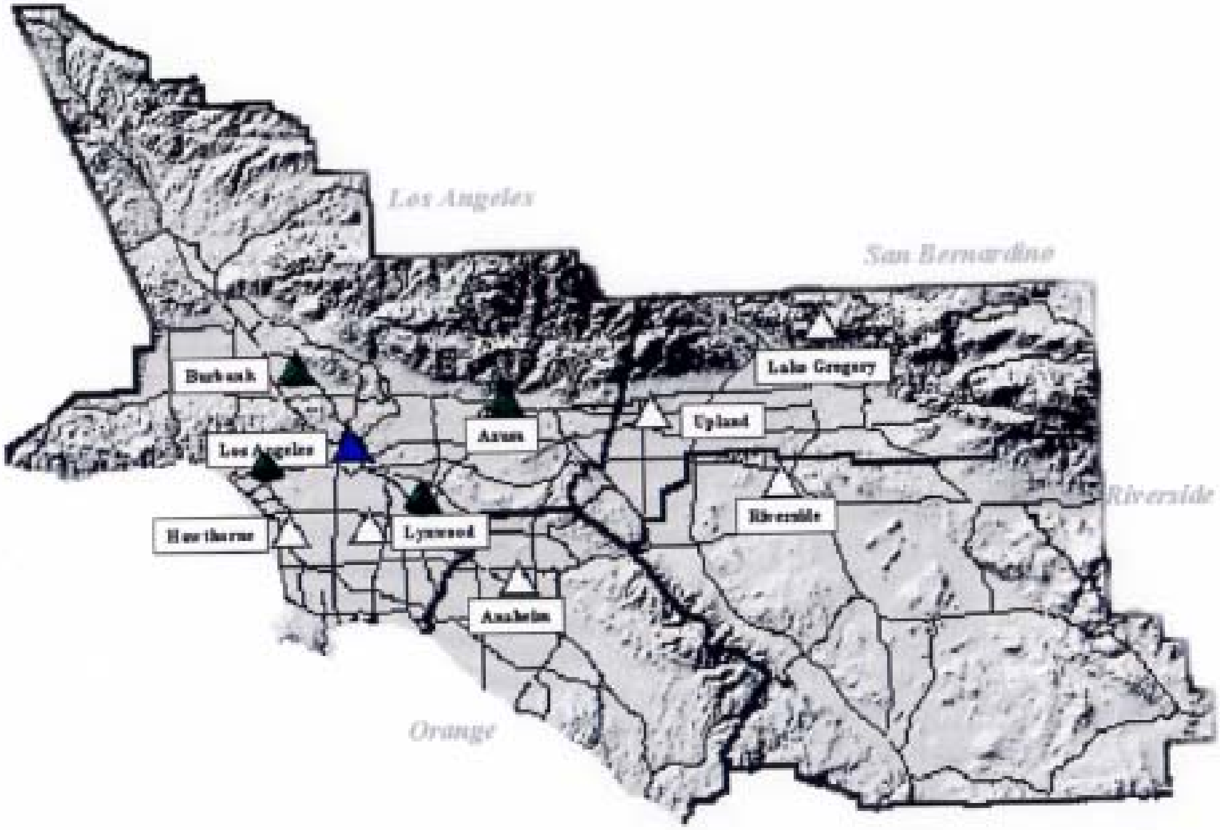
Field Measurements

- Sources
- Ambient air
  - Azusa
  - Burbank
  - UCLA
    - Winter
    - Summer

Diesel and Gasoline

Source	TNMOC/Sum of Speciated VOC's
Gasoline Vapor	1.07-1.09
Diesel Fuel Vapor	1.39-1.44
Diesel Exhaust	1.2 ± 0.2
range	1.0-1.6

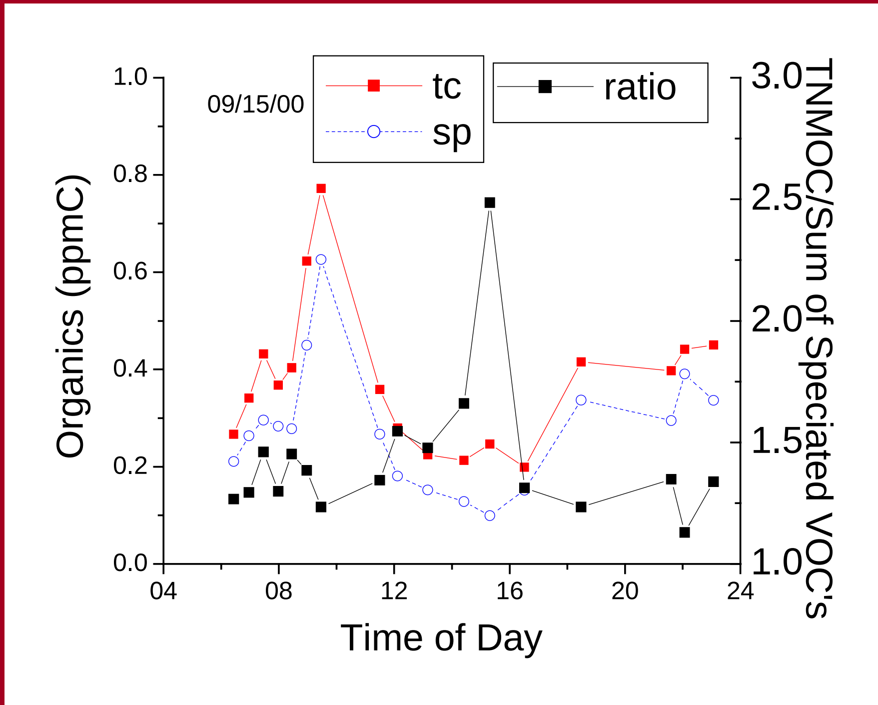
Figure 1-7. Map showing the major freeways and highways in the South Coast Air Basin as well as the locations of the "core" monitoring sites used in many of the analyses in this report.

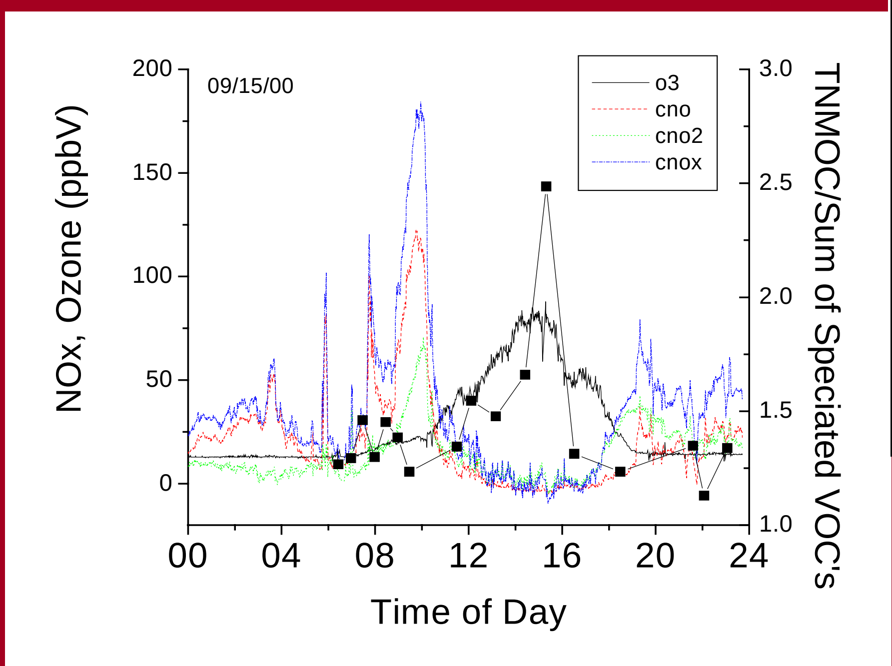


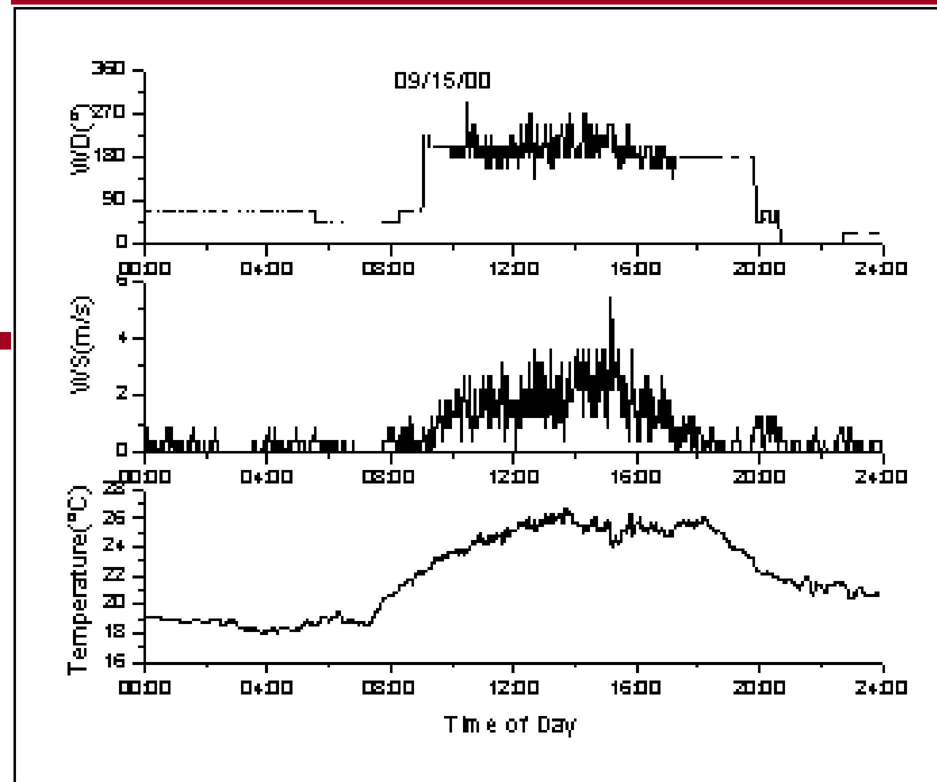
Instrumentation

Parameter	Instrument	Sampling Period (min.)	Sample frequency (1/h)	Sample volume /flow rate
TNMOC And VOC's	This work	10-20	1-2	500-1140 mL@50-57mL/min[1]
NO, NO_2, and NO_x	Thermo Environmental Model 42	1	60	100 mL/min 2 L/min
O_3	Dasibi Model 1003-RS	1	60	
Aerosols	Particle Measuring Systems LAS-X	1	60	200 mL/min
Windspeed, direction, Temperature	Davis Instruments Weather Wizard III	1	60	-

9/15/00 Friday







Field Data Summary

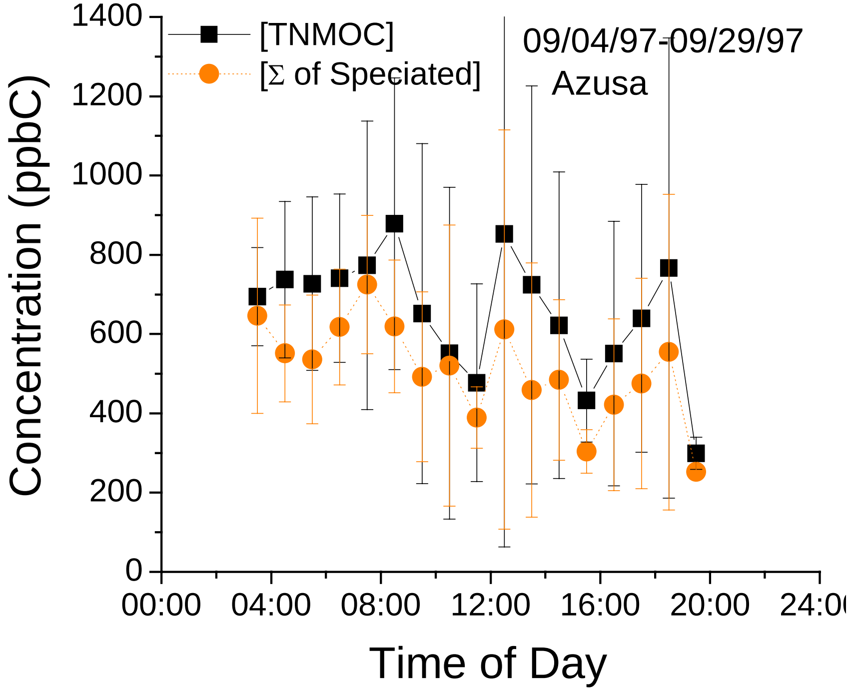
Site	Met.	TNMOC (ppbC)	Sum of Spec. VOC's (ppbC)	TNMOC/Sum of Speciated VOC's
Burbank Summer range 8/99	Clear	2300 ±250 740-4000	2070 ± 200 730-3000	1.11 ± 0.08 0.8-1.4
UCLA Summer range 8-9/99	Clear	426 ± 65 150-954	314 ± 42 166-622	1.37 ± 0.12 0.8-2.2
UCLA Summer range 9-10/00	Clear	377± 40 108-925	293 ± 31 85-713	1.30 ± 0.04 1.01-2.4
UCLA Summer range 9-10/00	Cloudy	229 ± 29 75-700	145 ± 21 45-529	1.65 ± 0.08 1.10-3.05
UCLA Winter range 11-12/00	Cloudy	317 ± 45 41-1047	295 ± 43 37-977	1.1 ± 0.03 1.0-1.96
Azusa Summer 9-10/1997	Clear	619 ± 37 201-1475	410 ± 26 242-966	1.26 ± 0.04 0.7-2.1

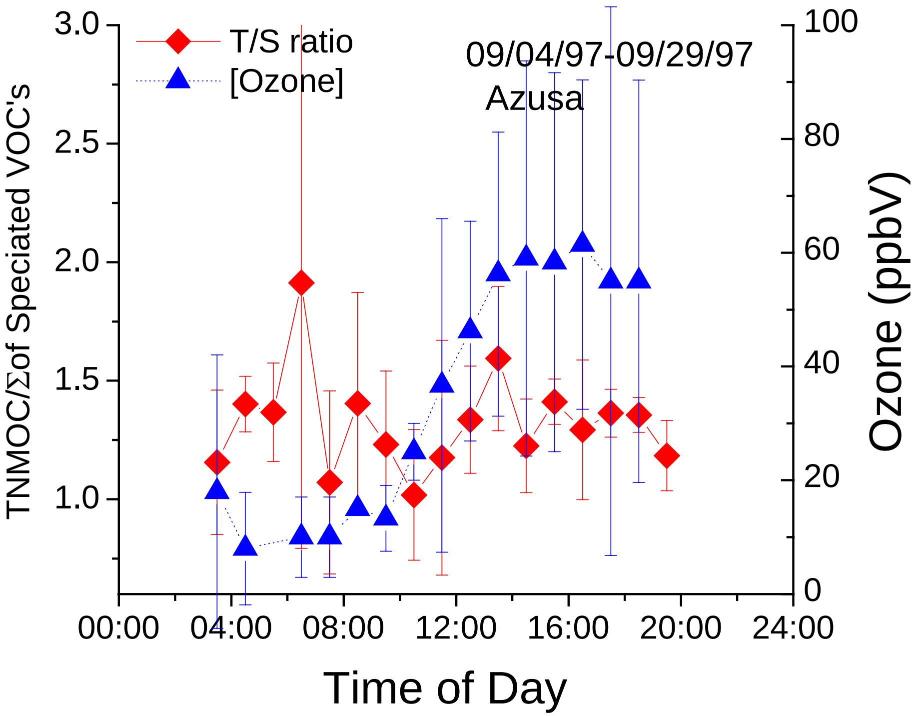
*All uncertainty ranges are $2\sigma_{mean}$

Literature “TNMOC”

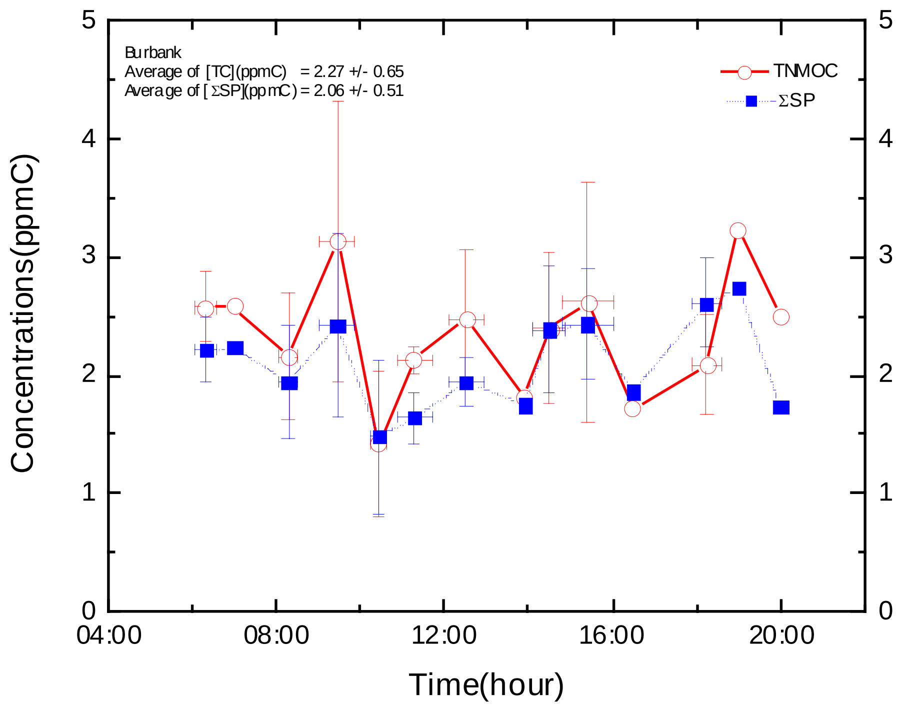
- Other measurements indicate there is a significant additional pool of VOC’s.
- Roberts et al. (1998) measured TNMOC/sum of speciated VOC’s ratios of 1.16 –1.36 in rural Nova Scotia using a related approach, in reasonable agreement with our results.
- Alastair et al. (2000) used 2-D GC to find hundreds of additional organics in the chromatogram baseline, with a T/S ratio of ~1.67 in Melbourne, Australia.
- Because their measurement used a GC column, it may have missed many compounds that we measure in our TNMOC channel.
- The cause for this discrepancy *may* be the selection of the speciated baseline.
- We set our baseline conservatively (low) to avoid overestimating the T/S ratio. With auto integrations, we get higher T/S ratios.
- Comparing TNMOC measurements to conventional GC data is tricky.

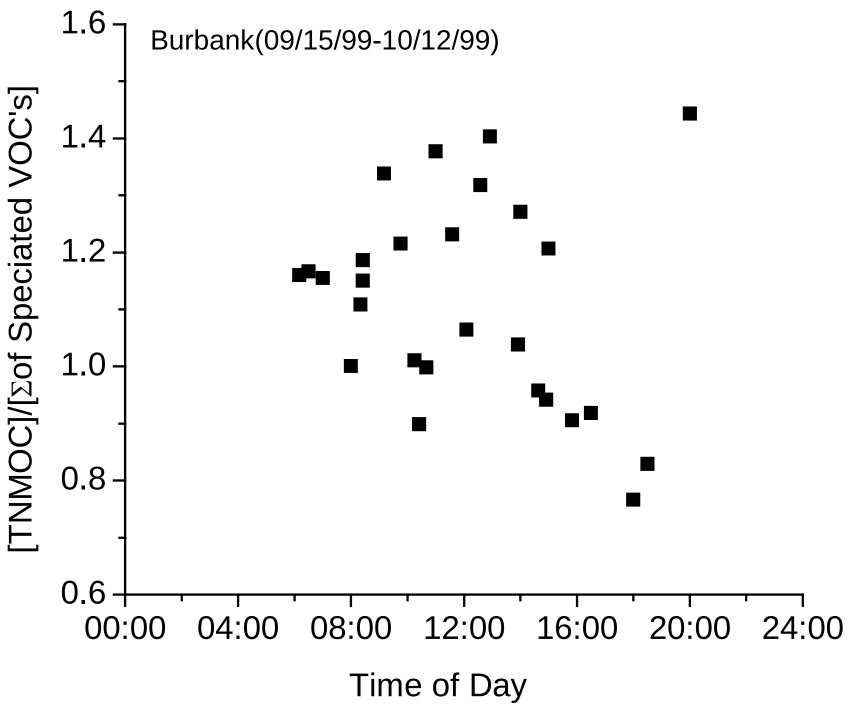
VOCs and T/S Ratio and Ozone at Azusa





VOCs and TNMOC/Sum of Speciated VOC's at Burbank



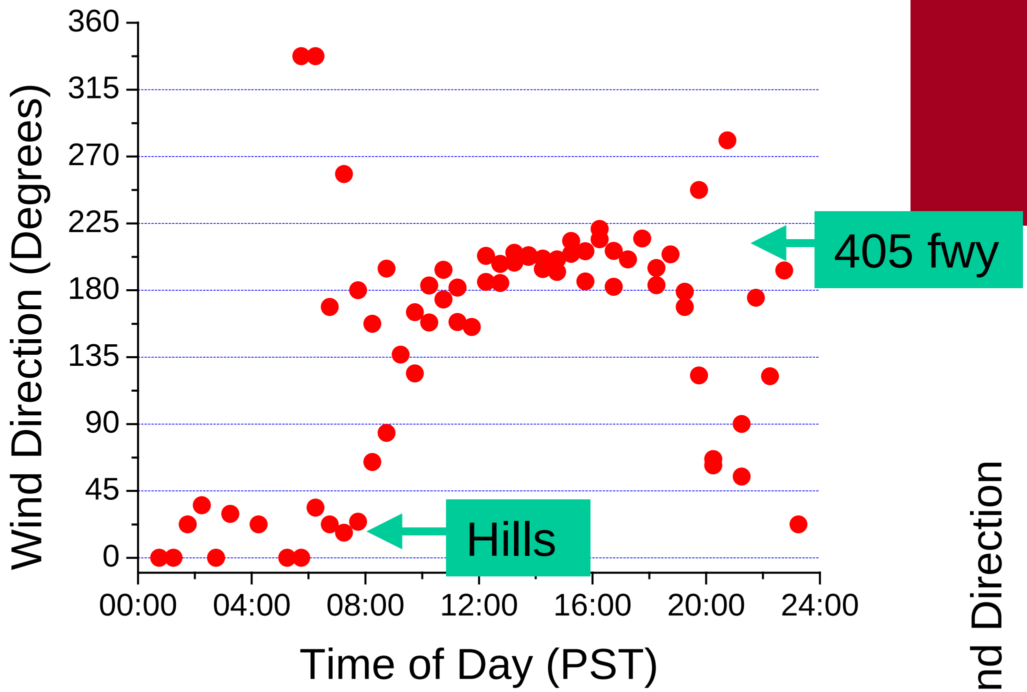


UCLA Clear vs. Cloudy

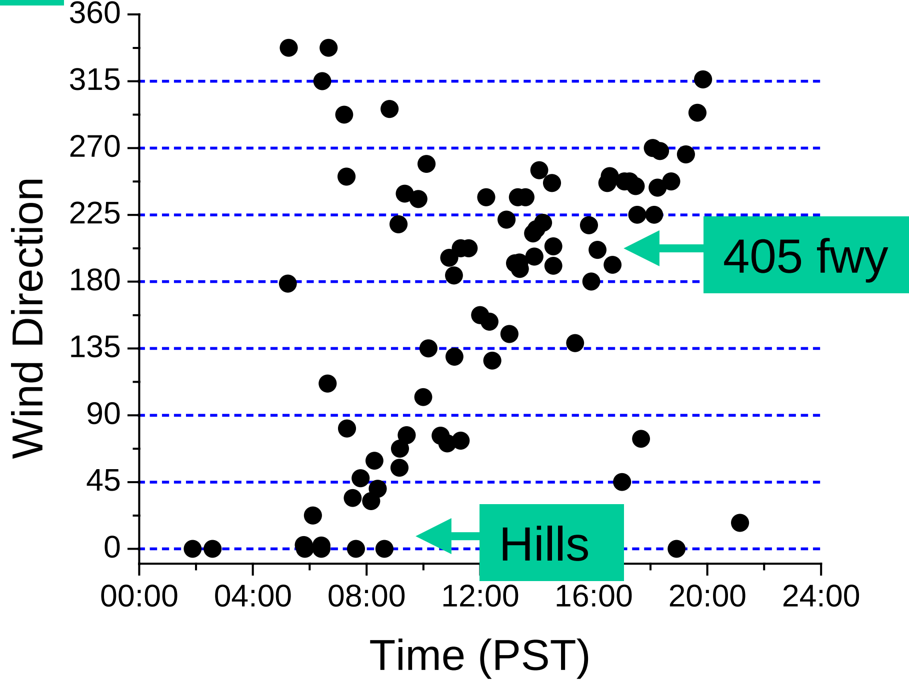
Met.	No. of Obser-vations		TNMOC (ppbC)	Sum of Spec. VOC's (ppbC)	T/S ratio	Avg. O_3 (ppbV)	Avg. Maximum O_3 (ppbV)
Clear	100	Average $2\sigma_{mean}$ range	377 40 108-925	293 31 85-713	1.30 0.04 1.01-2.4	36 σ = 22	75 σ =16 45-100
Cloudy	90	Average $2\sigma_{mean}$ range	229 25 75-700	145 17 45-529	1.65 0.08 1.1-3.05	42 σ = 17	61 σ = 13 41-79

UCLA Wind Direction

Summer



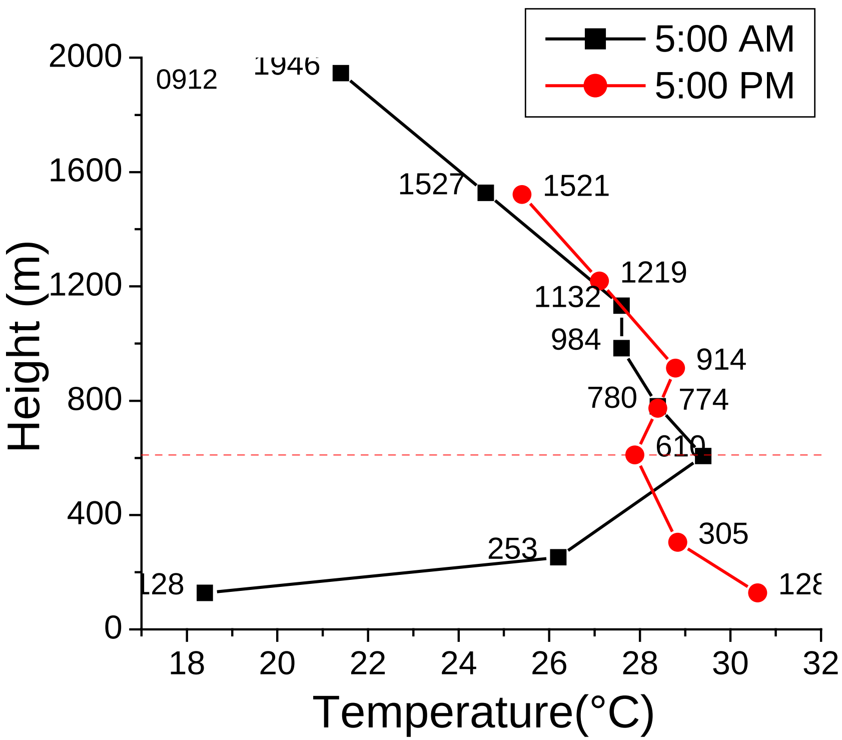
Winter



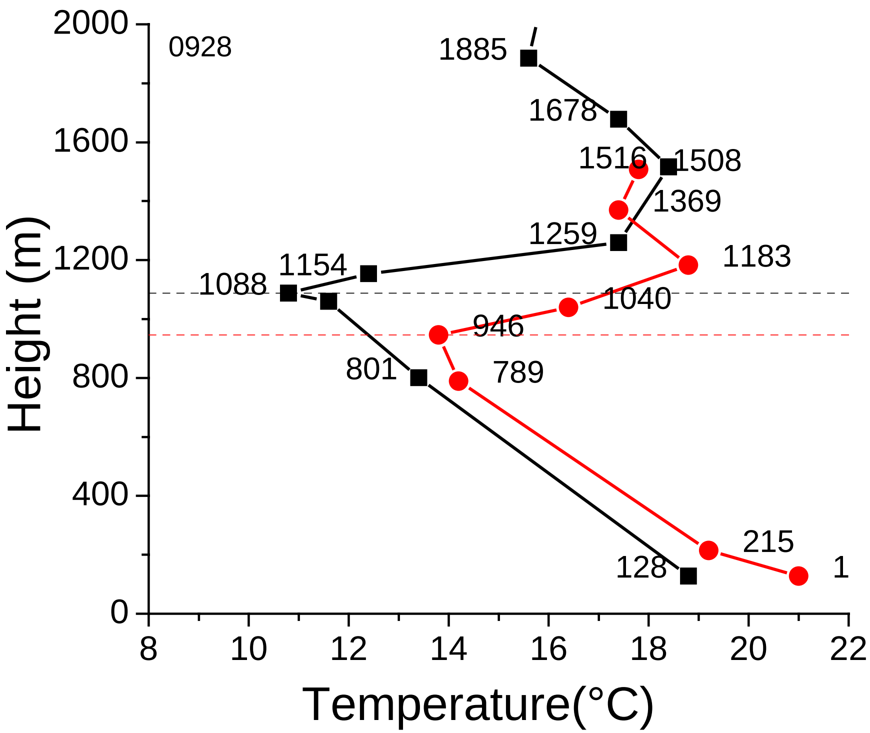
Atmospheric Temperature Structure

Summer

Clear



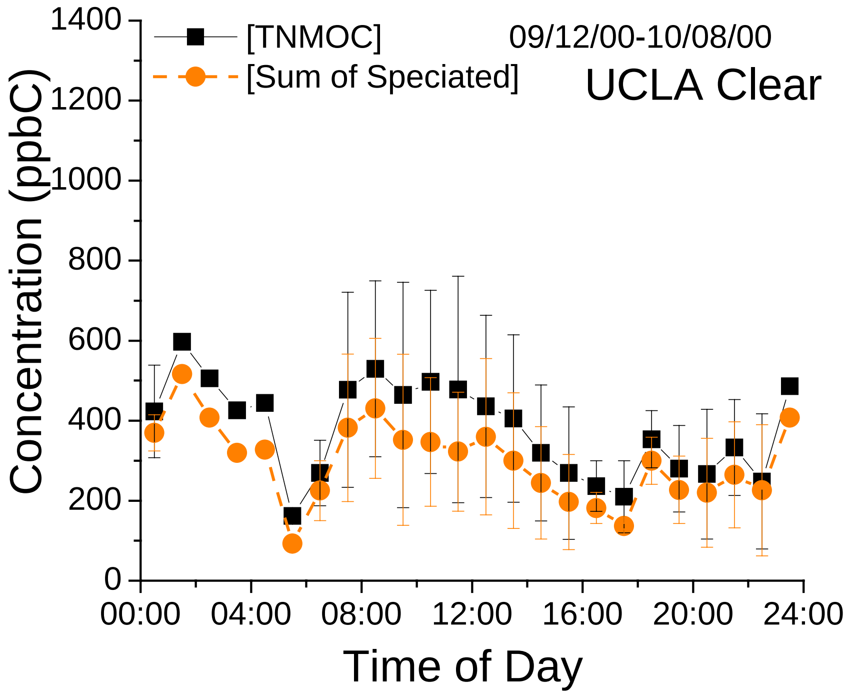
Cloudy

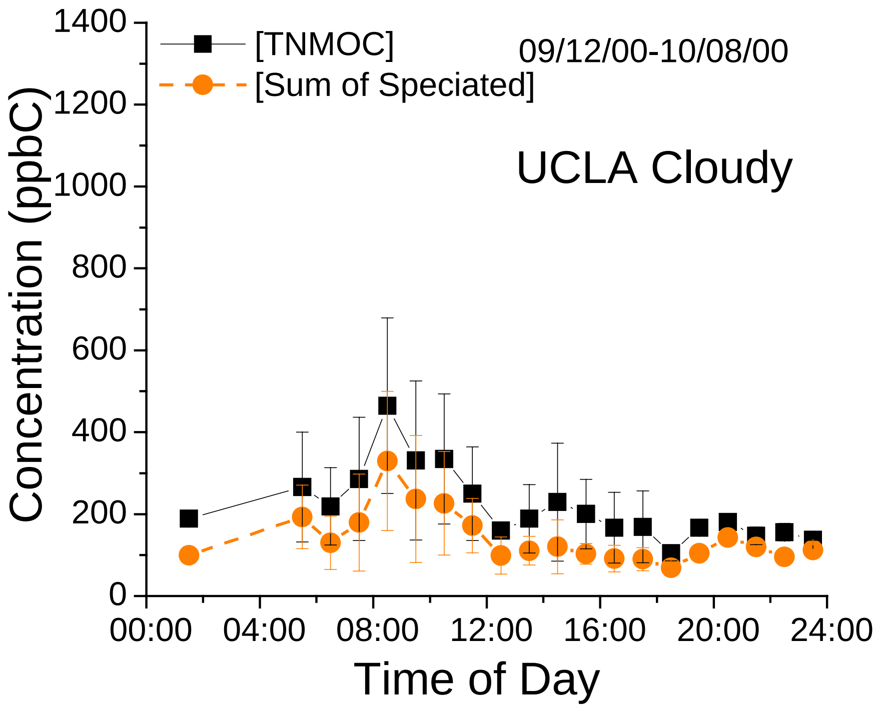


Early morning inversion, daytime shallow mixed layer

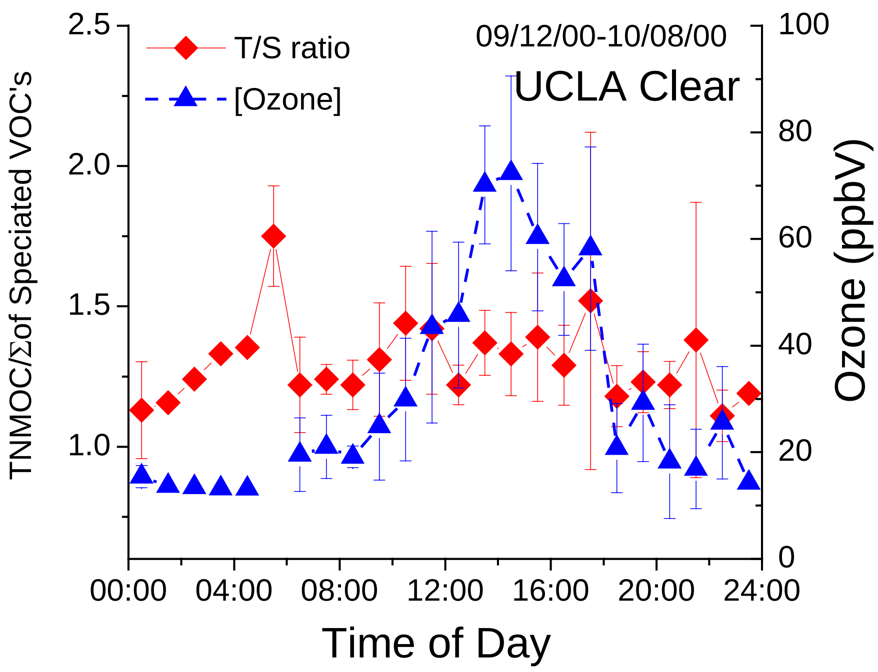
Deeper mixed layer, little diurnal temperature variation

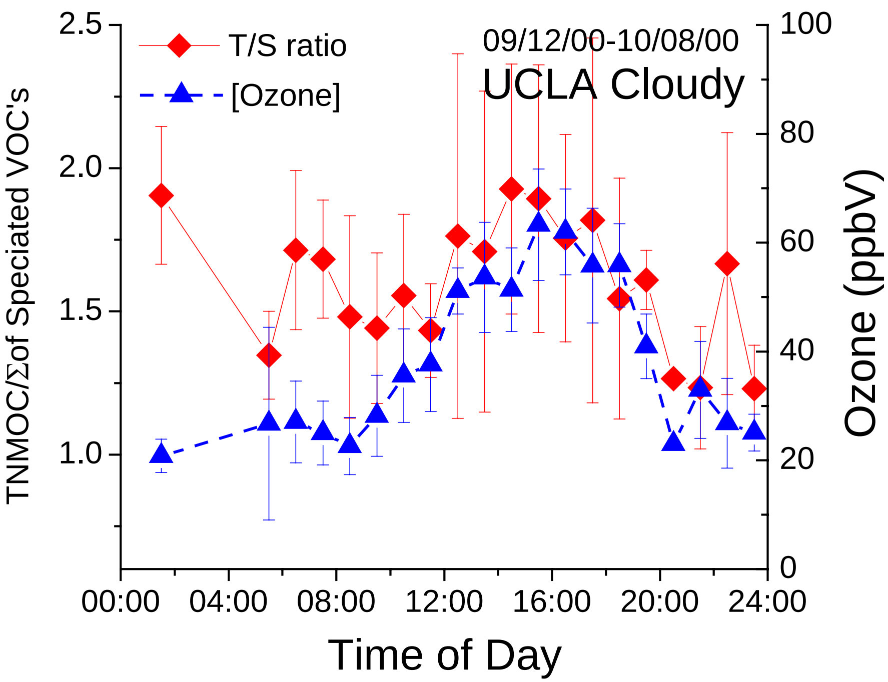
UCLA Clear and Cloudy VOC Concentrations





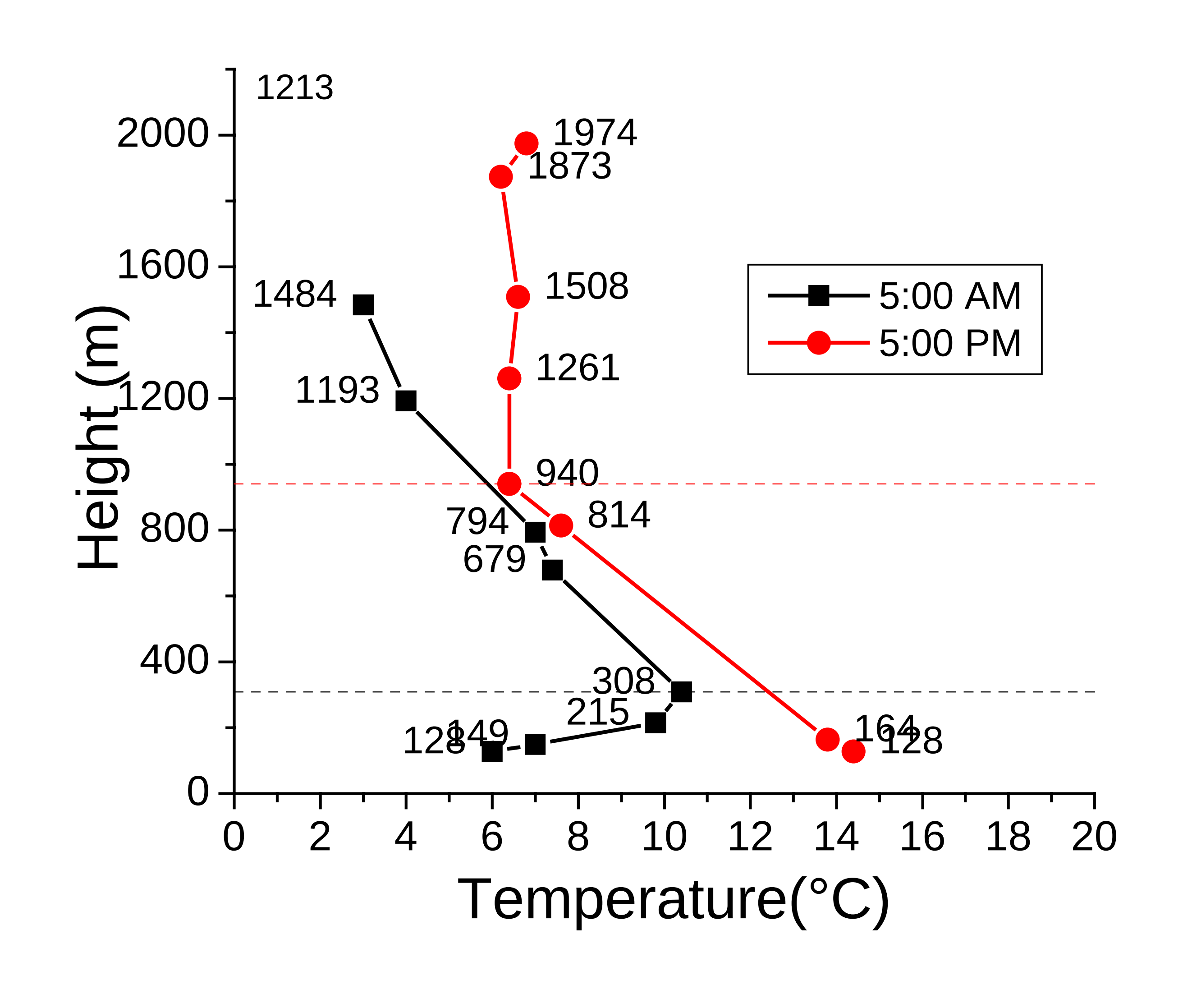
TNMOC/Sum of Speciated VOC's UCLA Clear and Cloudy



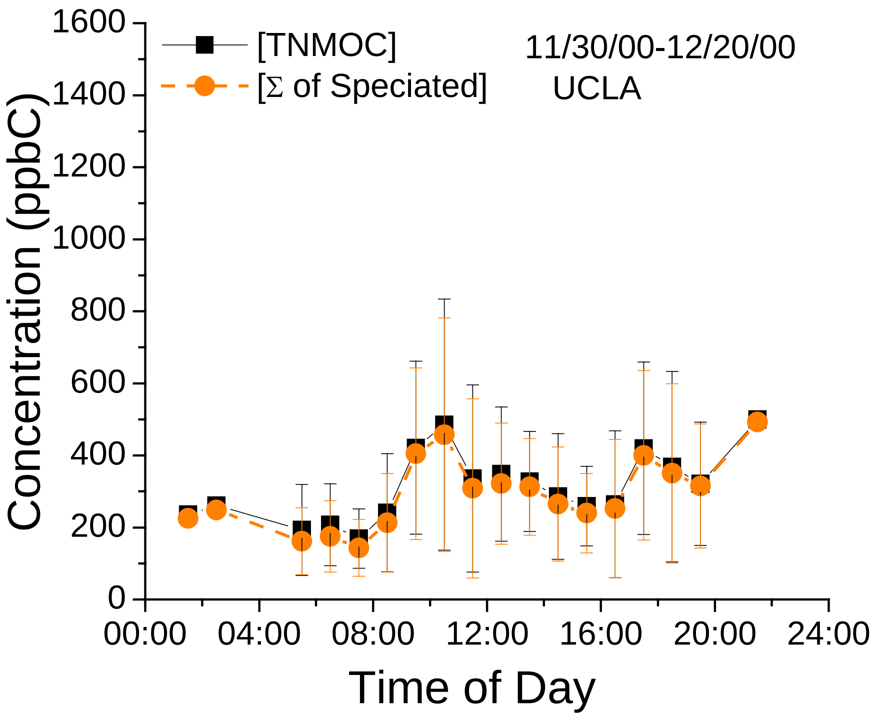


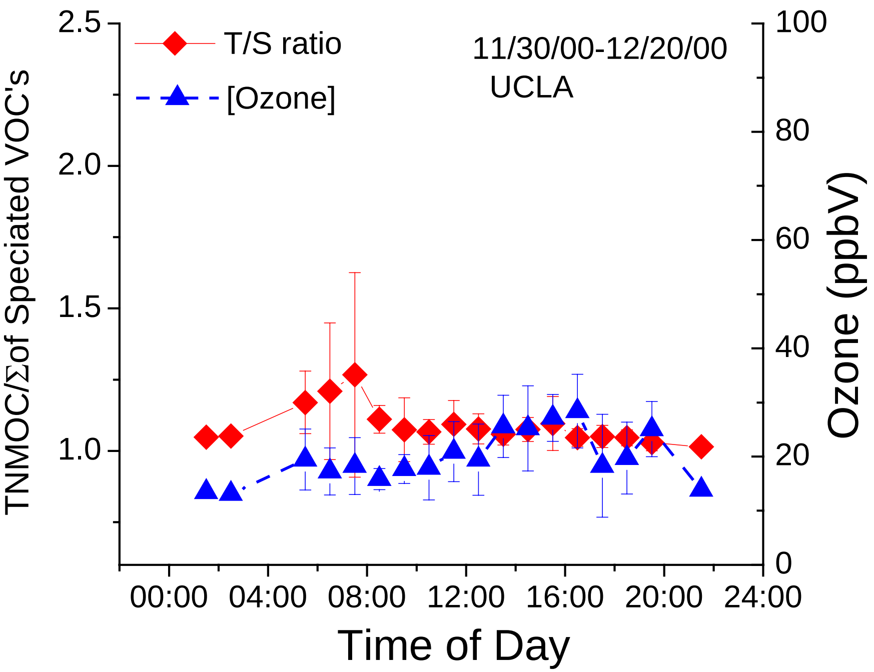
Atmospheric Temperature Structure

Winter



VOCs and T/S Ratio at UCLA-Winter





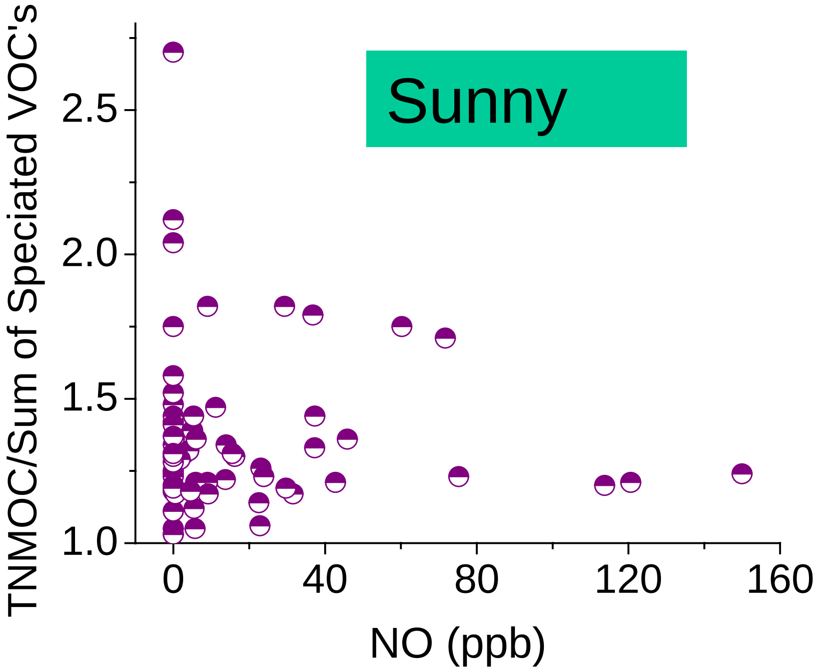
Correlations

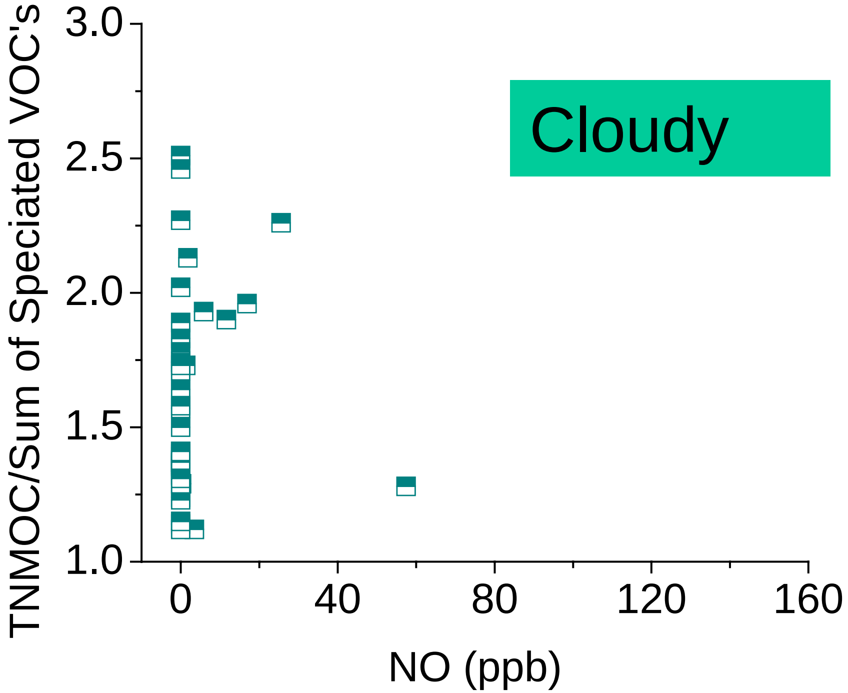
TNMOC/Sum of Speciated VOC's is not correlated with:

- O_3
- relative humidity
- wind speed or direction
- or for the most part time of day or day of week ("weekend effect").
- Weakly correlated with VOC concentration

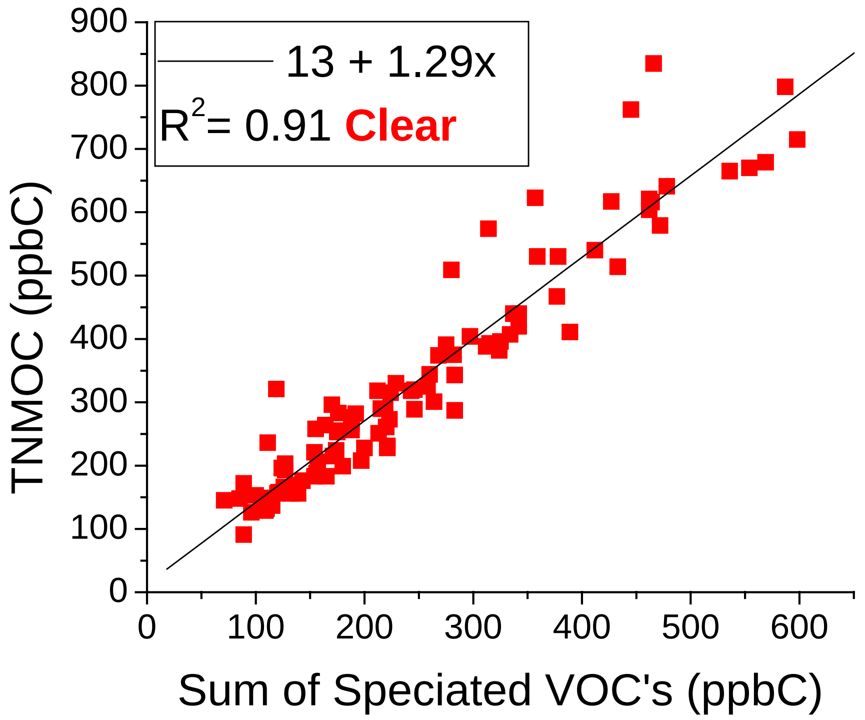
TNMOC/Sum of Speciated VOC's and NO

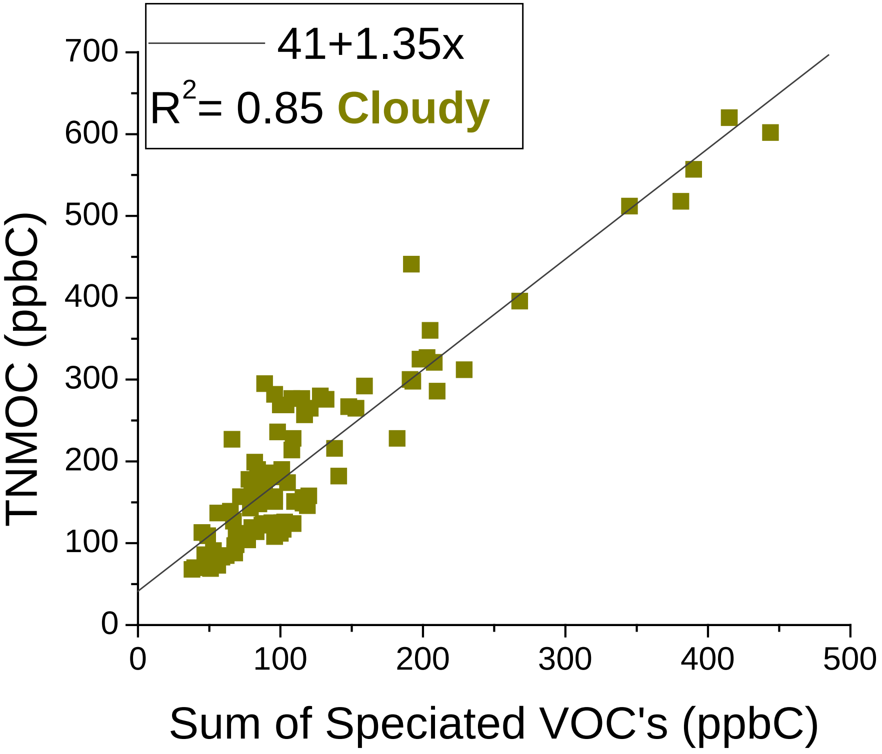
High TNMOC/sum of speciated VOC's are associated with low NO concentrations.





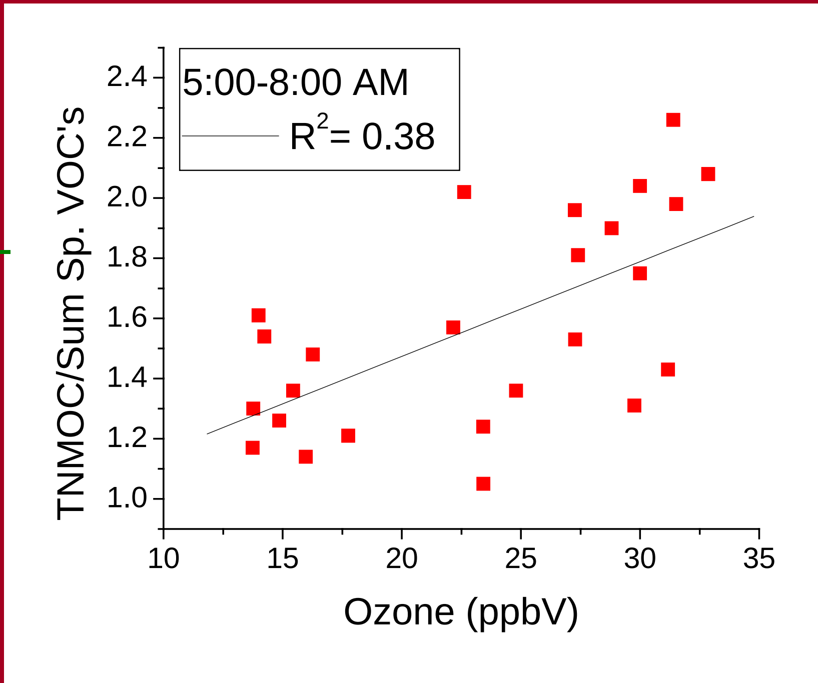
Relationship Between VOC Loading and T/S Ratio





T/S Ratio and Ozone

Site	R^2 for Correlation with Ozone
Azusa 1997	N/C
UCLA Summer 1999	0.19
Burbank Summer 1999	N/C, Negative trend
UCLA Summer 2000 Clear	0.11
UCLA Summer 2000 Cloudy	N/C
UCLA Winter	N/C Negative trend
UCLA Summer 5:00-8:00AM	0.38



Photochemical Processing:

Estimating Photochemical Age

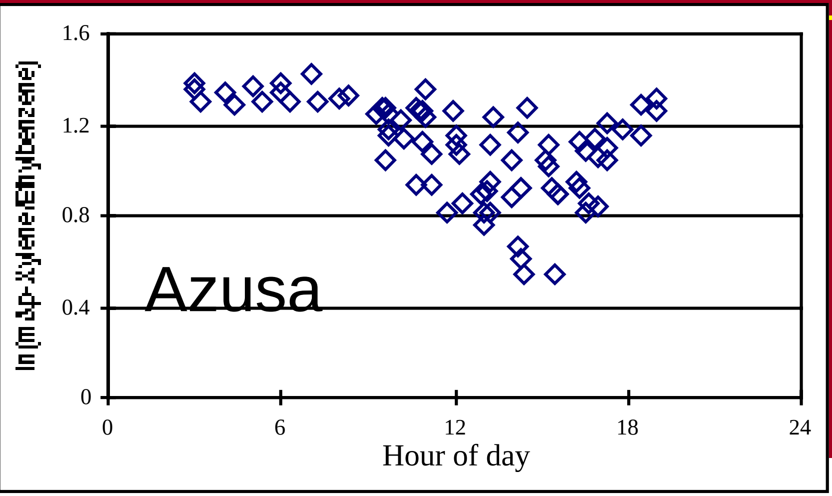
-Pairs of aromatics with different lifetimes can be used as markers of photochemical processing.

-The best are aromatics that are emitted in constant ratios regardless of source.

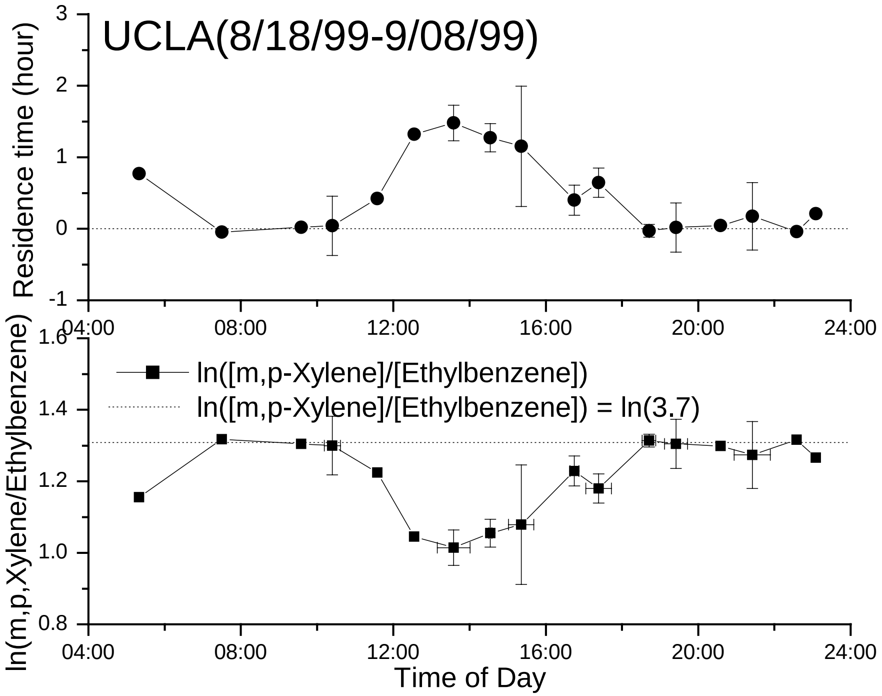
-m,p-Xylene and ethylbenzene are typically correlated with $R^2 < 0.95$.

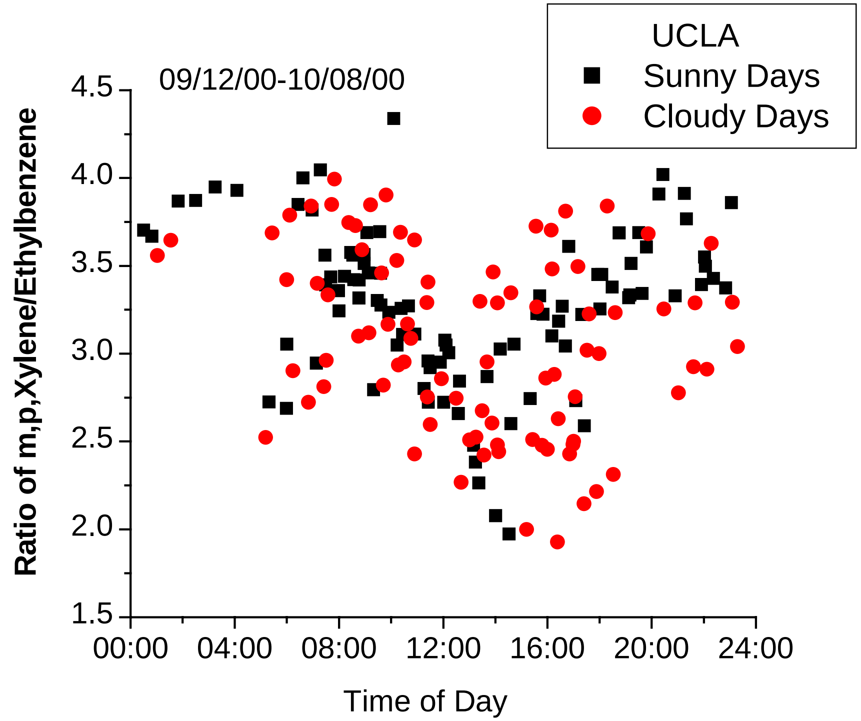
Compound	K_{OH}	Lifetime (hrs)
Benzene	1.23	75
Toluene	5.96	15
Ethylbenzene	7.1	13
m-Xylene	23.6	4
p-Xylene	14.3	6.5
o-Xylene	13.7	6.8

Air Mass Age



Aromatics indicate maximum average photochemical processing times of 2-4 hours.





T/S Ratio and Photochemical Processing

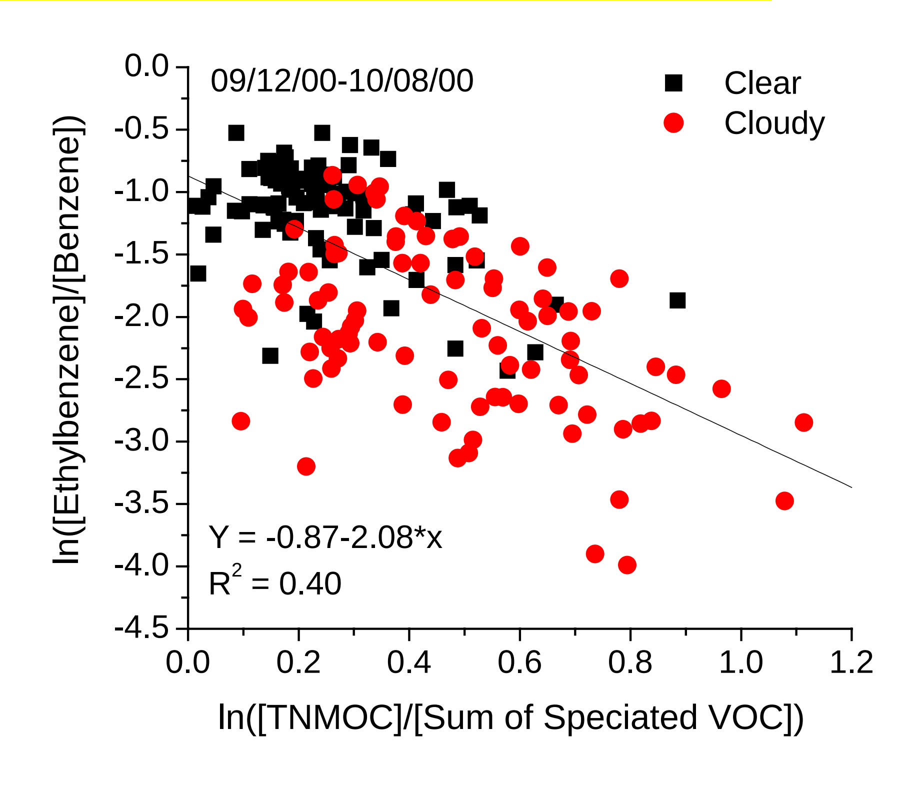
- Assume:
  - Average speciated mixture of 100 hydrocarbons from the EPA for 29 cities at 6-9 AM survey (Jeffries 1995).
  - Rate constants for each hydrocarbon reacting with OH, and for alkenes with ozone (Atkinson, 1997).
  - 0.1 ppt OH (2.5 $\times$ 10^6 molec cm^3) and 50 ppbv O_3 for 4 hours.
  - $$A = A_0 \exp(-(k_{OH}[OH] + k_{O3}[O_3])t)$$

T/S Ratio and Photochemical Processing, continued

- Then:
  - 30% of the hydrocarbons react once with either OH or ozone.
  - The organics have an average of 7 carbons, and add ~1.5 functional groups (alcohol, carbonyl, or nitrate) per reaction.
  - The total mix increases its heteroatom content relative to the carbon content by about 7%.
  - The effect of this increase on the T/S ratio cannot be calculated precisely; heteroatoms either reduce the FID response or cause the compound to be lost or broadened in the column.
  - The T/S ratio should have little dependence on the time of day or ozone.

UCLA Aromatic Correlations

Compound	K_{OH}	Lifetime (hrs)
Benzene	1.23	75
Toluene	5.96	15
Ethylbenzene	7.1	13
m-Xylene	23.6	4
p-Xylene	14.3	6.5
o-Xylene	13.7	6.8



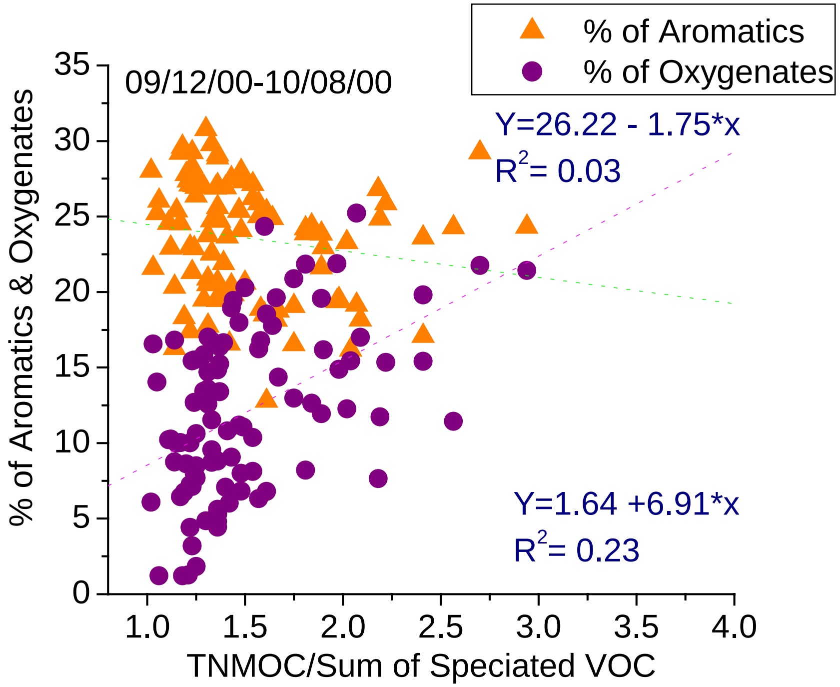
Period	UCLA2000		
Aromatic Ratio	R^2 w/ self	R^2 w/ O_3	R^2 w/ T/S
ln(Ethylbenzene/Benzene)	0.48	0.13	0.40
ln(Toluene/Benzene)	0.46	0.19	0.36
ln(o-Xylene/Benzene)	0.48	0.23	0.34
ln(m,p-Xylene/ Ethylbenzene)	0.99	0.49	0.03

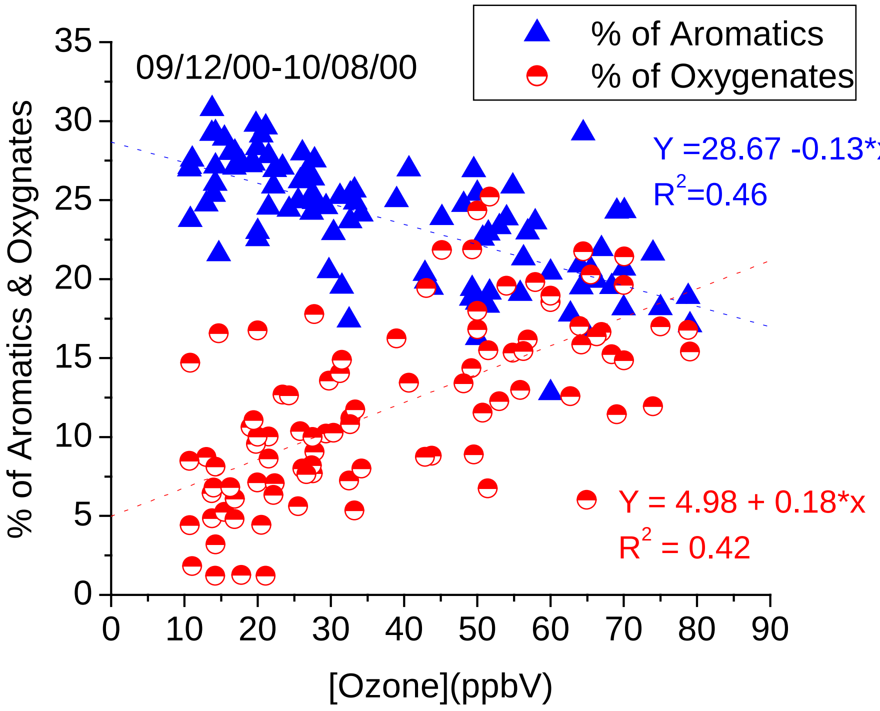
Contribution of Light Oxygenates: Azusa

Oxygenate	Average Concentra-tion (ppbC)	Percent of TNMOC	FID Response Factor (RF = 1 per C in NMHC's)
Acetaldehyde	8.4	1.8	1.65
Methanol	6	1.3	0.77
Ethanol	11	2.4	1.02
Sum	25	5.5	
TNMOC meas. in Spec. channel (%)			3.7

Light Oxygenates at UCLA

Average propanal + acetone would result in a T/S ratio of ~1.08; observed ratio is 1.45 for clear and cloudy combined.





Conclusions

- Standard VOC measurement underestimates VOC level typically by 10-60%, total can be up to 3x higher than the sum of speciated VOC's.
- Excess varies strongly with location, day of week and meteorology.
- At UCLA, large excess TNMOC is strongly associated with either high mixing heights (summer) or strong nighttime inversions coupled with less influence from sources.
- Reduced FID response of oxygenates does not account for much of the excess organics.
- Excess organics appear to be associated with photochemical activity and with mixing from aloft.
- Chemical identity and source of excess VOC's is still to be determined.

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