

Rathdrum Prairie Ozone Precursor Study

Final Report

Prepared by

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PREFACE

This Final Report is submitted by the Laboratory for Atmospheric Research at Washington State University as part of a contract project through Idaho Department of Environmental Quality (IDEQ) to conduct measurements of volatile organic compounds, CO, O₃, and NO_x at two IDEQ air quality monitoring sites in the Rathdrum Prairie region of northern Idaho.

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1. INTRODUCTION

Washington State University deployed and operated a proton transfer mass spectrometer (PTR-MS), a CO monitor, an O₃ monitor, a NO_x monitor, and ATEC canister samplers at two monitoring sites in the Rathdrum Prairie region of Idaho from August 26 to September 9, 2008. The purpose of these measurements was to evaluate ozone precursor concentrations and VOC / NO_x ratios.

2. FIELD SET-UP AND OPERATION

2.1 Site Description

Air monitoring was performed at two sites: Post Falls (PF) and Lancaster (LCR). Both sites were existing IDEQ monitoring sites. The LCR site had existing monitors for O₃ and NO_x operated by IDEQ. A portable EKTO trailer supplied by IDEQ was moved to the PF site to house WSU equipment. The existing EKTO shelter at LCR was used to house the WSU equipment. At the Post Falls site air, outside air was pulled through a ½" PFA tube extending ~ 5 feet above the roof of the trailer by a blower inside the trailer. The PTR-MS, O₃, CO, NO_x monitors, and canister samplers sub-sampled from this flow via a glass manifold. At the Lancaster Site, the PTR-MS, CO instrument, and canister samplers sub-sampled from the existing air sampling manifold. An overview map showing the proximity of these sites to industrial sources of VOCs and NO_x in the Rathdrum Prairie is shown in Figure 1a.

The Post Falls site is in a residential neighborhood in Post Falls. Figure 1b shows a map of the immediate area around the site. The site is located in an empty corner lot at 1357 N Syringa Street (47° 43' 17" N , 116 ° 55' 37" W). The lot is fenced and contains a water supply well operated by the city. The lot is about 200 feet per side. The sampling trailer was located in the southwest corner of the lot, a point furthest away from the bordering streets. The lot is bordered by residential homes to the south and west, and by low traffic residential streets to the north and east. I-90 is located 0.6 miles due south.

The Lancaster Site is in a rural area on Lancaster Road. Figure 1c shows a detailed map of the local area around the site.. The trailer is located in a fenced lot that houses a water supply well about 200 feet from the road. The immediate surrounding area is agricultural. The site is located about a mile to the north east from the Cour d'Alene regional airport. Sate highway 95 is located 0.75 miles west. The highway runs north south and the stretch of highway from the town of Hayden, 1 mile south of the site, to Cour D'Alene is developed.

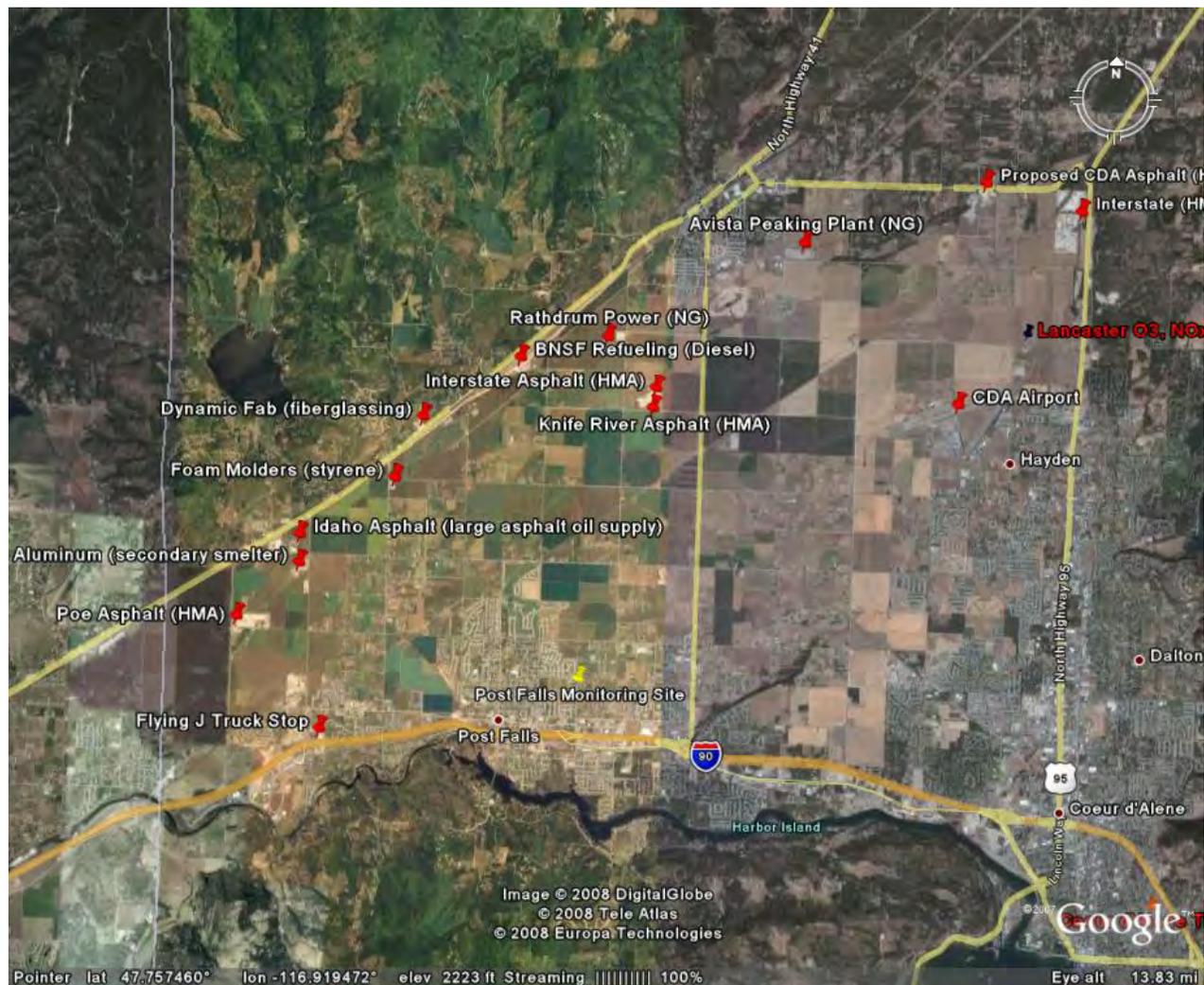


Figure 1a. Overview map of Rathdrum Prairie sampling area showing the Post Falls and Lancaster sampling sites and potential industry sources.

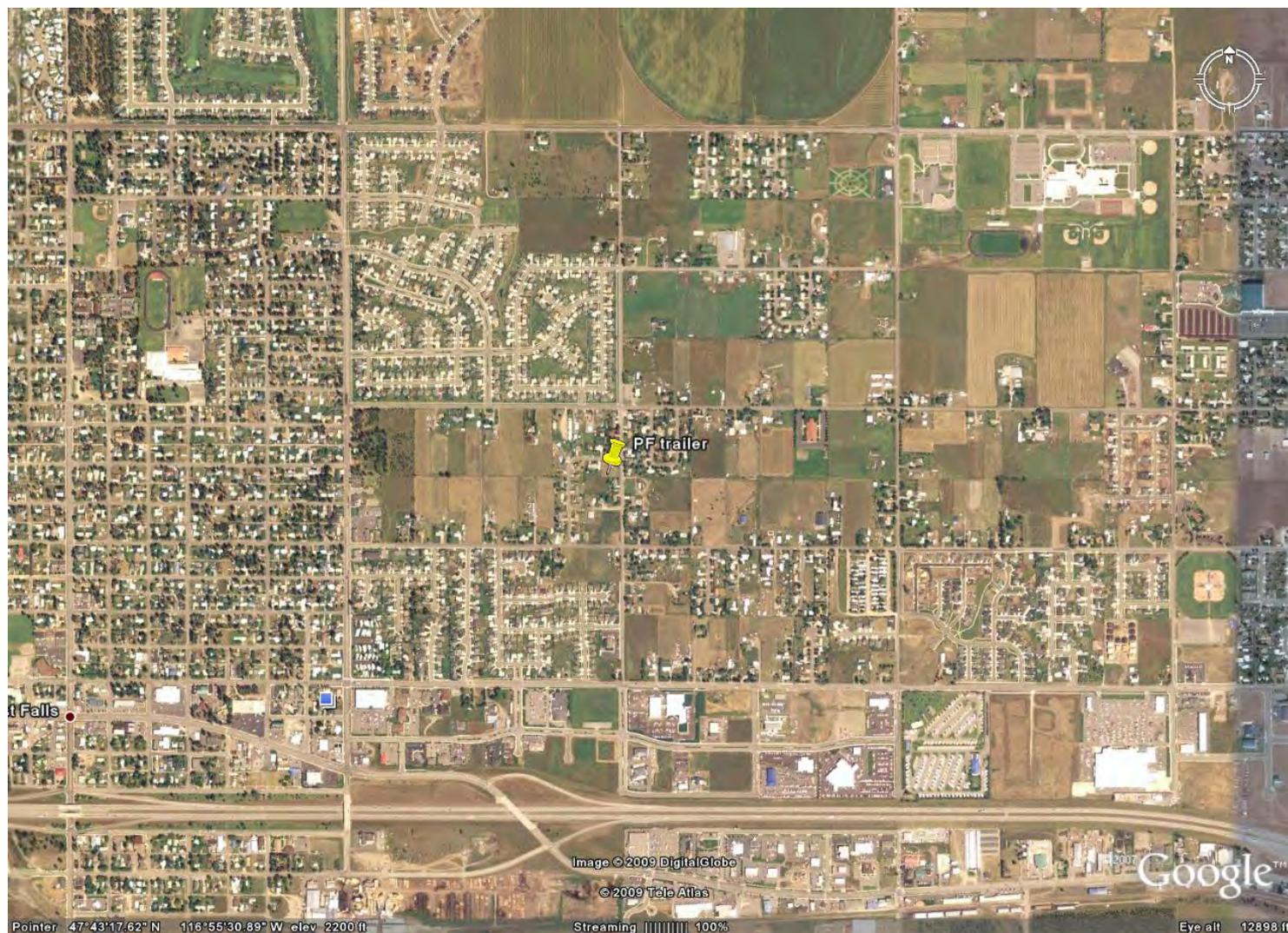
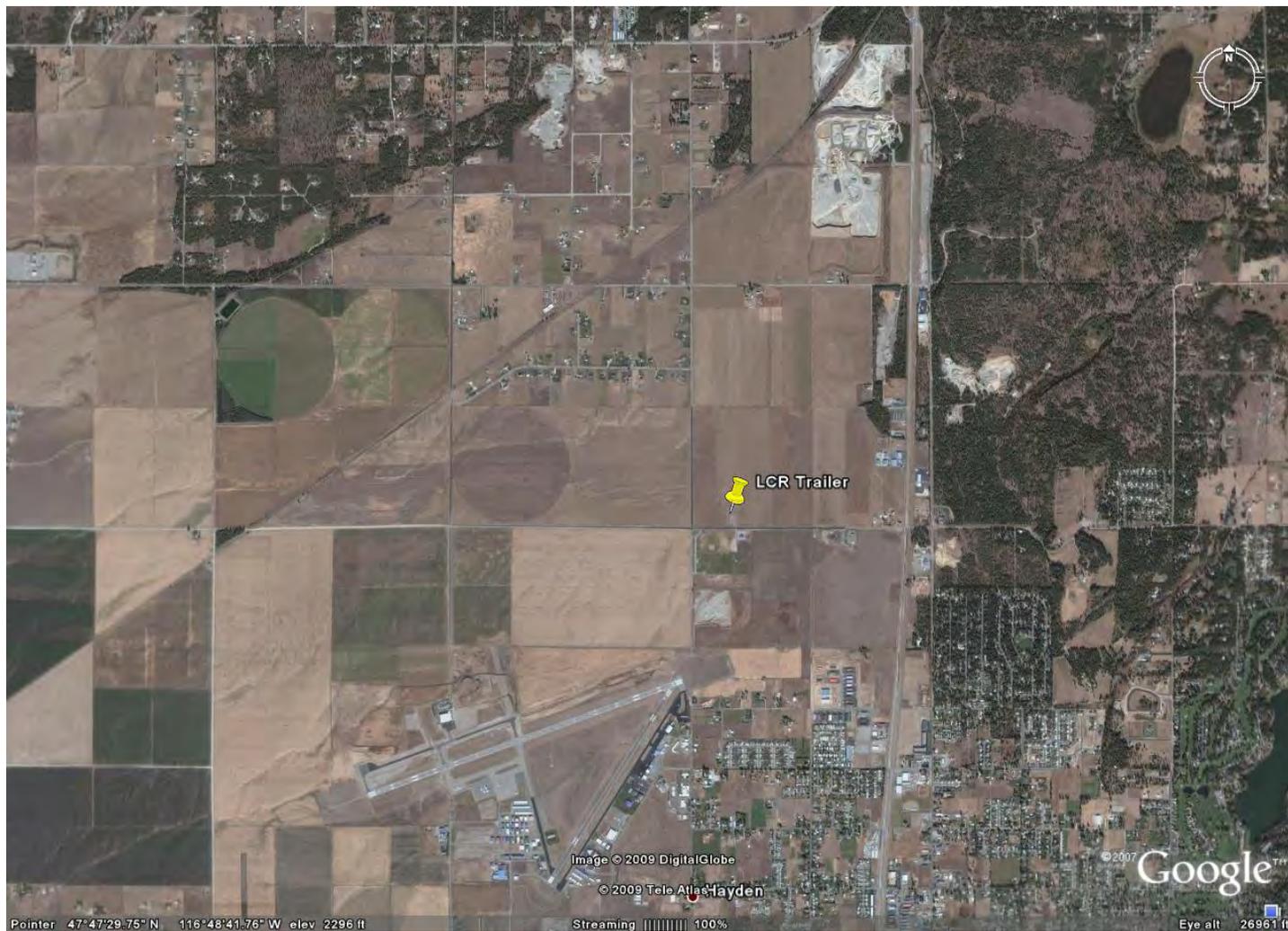


Figure 1b. Detail map of Post Falls sampling site.



1c. Detail map of Lancaster sampling site.

2.2 Canister Sampling

Canister sampling systems were set-up at both sites on August 26. Canister sampling was performed with ATEC automated canister samplers that filled evacuated canisters at predetermined times. Three ATEC single channel canister samplers were supplied by IDEQ and one ATEC sampler was borrowed from the Environmental Restoration & Waste Management Division of the Nez Perce tribe. There were two samplers at each site: 1 sampler for a morning canister fill from 6 to 9 AM to characterize traffic emissions, and 1 sampler for an afternoon sample from 3 to 5 PM. The samplers provided a constant mass flow over this time period. This flow was set so the canister was pressurized to about 25 psia at the end of the sampling period. The final pressure was dependent on the sampler. IDEQ personnel (Shawn Sweetapple and Scott Hondel) exchanged the canisters when WSU personnel were not on-site. Canisters were returned to WSU for analysis of C₂-C₁₀ hydrocarbons. The canisters were analyzed for the 48 species listed in Table 1.

Table 1. Analytes for Canister Analysis

Alkanes	Alkenes	Alkynes	Aromatics
ethane	ethene	acetylene	benzene
propane	propene		toluene
i-butane	T-2-butene		ethylbenzene
n-butane	1-butene		m,p-xylene
2,2-dimethylpropane	2-methylpropene		o-xylene
cyclopentane	C-2-butene		1,3,5-trimethylbenzene
i-pentane	cyclopentene		1,2,4-trimethylbenzene
n-pentane	2-methyl-2-butene		1,2,3-trimethylbenzene
methylcyclopentane	T-2-pentene		i-propylbenzene
cyclohexane	3-methyl-1-butene		2-ethyltoluene
2,2-dimethylbutane	1-pentene		3-ethyltoluene
2-methylpentane	isoprene		4-ethyltoluene
3-methylpentane	alpha-pinene		
hexane	beta-pinene		
2,3-dimethylpentane			
2-methylhexane			
3-methylhexane			
heptane			
2,2,4-trimethylpentane			
2,3,4-trimethylpentane			
octane			

2.3 NO_x, O₃, CO monitors

The NO_x, CO, and O₃ monitors were initially set-up at the Post Falls site on August 26. On September 2 the CO monitor was moved to the Lancaster site along with the PTR-MS.

CO was measured with a TECO 48 CO analyzer. The instrument was spanned by diluting a 20 ppmV standard from Scott Specialty gas with zero air. NO_x was measured with a TECO 42C analyzer. The instrument was spanned by diluting a 48 ppmV standard from Scott Specialty gas with zero air. O₃ was measured with a Dasibi 1008 ozone analyzer. It was calibrated against a Dasibi PC-1008 ozone calibrator. This calibrator was re-certified by the Idaho Department of Health and Welfare CARB standard in December 2008. Analog output signals from these monitors were recorded using a LabJack U3 data acquisition hardware (LabJack Inc) and DaqFactory software (Azeotech Inc).

2.4 PTR-MS

Ambient air monitoring with the PTR-MS was done first at Post Falls and then the Lancaster site. The PTR-MS was operated to measure the species shown in Table 2. Each ion was measured sequentially for 2 seconds; the entire sequence of measurements repeated every 58 seconds. The PTR-MS was calibrated with a multicomponent gas mixture (Scott-Marrin) diluted with zero air to ~ 20 ppbv range. The species in this gas mixture are highlighted in bold in Table 2. The formaldehyde, formic acid, and acetic acid measurements were exploratory in nature to evaluate PTR-MS measurements of these species and these data are not reported. The PTR-MS automatically performed a zero and span every 8 hours.

Table 2. Compounds measured by PTR-MS for the Rathdrum Prairie Ozone Study

Ion m/z	Species	Description
31	Formaldehyde	photoproduct
33	Methanol	solvent, biogenic emissions
42	Acetonitrile	wood smoke tracer
43	propene + organic fragments	general tracer of organics
45	Acetaldehyde	photoproduct
47	formic acid	photoproduct?
59	Acetone	solvent
61	acetic acid, glycoaldehyde	photoproduct?
69	Isoprene	biogenic
71	methcrolein + methylvinylketone	isoprene photoproducts
73	2-butanone	solvent
79	Benzene	autoexhaust
93	Toluene	autoexhaust
105	Styrene	industrial
107	C₂ benzenes (C₈H₁₀)	autoexhaust
121	C₃ benzenes (C₉H₁₂)	autoexhaust
129	Naphthalene	diesel exhaust, asphalt plant tracer
135	C₄ benzenes (C₁₀H₁₄)	autoexhaust
137, 81	Monoterpenes	biogenic
139	Nopinone	β-pinene oxidation product

2.5 Timeline of Events

A time table showing the sampling schedule is shown in Table 3. The numbers in the canister sampling columns indicate the number of canister samples collected in that time period. Duplicate canister samples (were collected on the last day of the field experiment at each site (2 AM samples at Post falls, 2 PM samples at Lancaster). The instruments were deployed such that for the study there were measurements of O₃ and NO_x and both sites over the study period. The PTR-MS and CO instrument spent the first half of the study period at Post Falls, and the second half at Lancaster.

Table 3. Schedule of WSU Measurement Activities

Date	Day	WSU Activity	Post Falls					Lancaster					
			Canister Sampling		PTR-MS (WSU)	CO (WSU)	NOx (WSU)	O3 (WSU)	Canister Sampling		PTR-MS (WSU)	CO (WSU)	NOx & O3 (IDEQ)
			AM	PM					AM	PM			
Aug 26	Tues	Set-up PF				x	x	x					x
27	Wed	PF	1	1	x	x	x	x					x
28	Thur	PF	1	1	x	x	x	x		1			x
29	Fri	PF	1	1	x	x	x	x	1				x
30	Sat	PF	1	1	x	x	x	x	1	1			x
31	Sun	PF	1	1	x	x	x	x	1	1			x
Sept 1	Mon	PF	1	1	x	x	x	x	1	1			x
2	Tues	Move to LCR	1	1	x		x	x	1	1		x	x
3	Wed	LCR	1	1			x	x	1	1	x	x	x
4	Thur	LCR	1	1			x	x	1	1	x	x	x
5	Fri	LCR	1	1			x	x	1	1	x	x	x
6	Sat	LCR					x	x			x	x	x
7	Sun	LCR					x	x			x	x	x
8	Mon	LCR	2				x	x		2	x	x	x
9	Tue	pack-up											

2.6 Instrument Performance

The PTR-MS had some performance problems at the Post Falls site. The problems were traced to temperature variations of the instrument which impacted the ion source and the generation of the reagent ion H_3O^+ . The PTR-MS is sensitive to variations in instrument temperature because of the way the instrument's ion source operates. To generate the H_3O^+ reagent ion, the ion source is supplied by a low flow of water vapor controlled by a mass flow controller. The source of water vapor is a stainless steel bottle filled with distilled water. When temperatures cycled in the instrument due to shelter temperature changes from day to night water condensed in the mass flow controller causing flow variability and an erratic reagent ion signal. The end result was low sensitivity of the instrument due to low reagent ion count rates and unwanted ions such as O_2^+ being generated in the ion source. This problem became manifest at ~ 21:45 PM on August 29 and the instrument was not working properly again until 14:00 on August 30. After August 31 the sensitivity of the instrument was much reduced again, due to sudden decrease in reagent ion count rates, 2×10^5 Hz compared to normal operating conditions of 5×10^6 Hz. The PTR-MS data are noisier and detection limits much higher than normal. This was likely due to a water flow vapor problem to the ion source. Figure 2 shows a time series of the PTR-MS toluene data from Post Falls to illustrate the change in signal-to-noise when the reagent ion count rates fell to 2×10^5 Hz during the last several days of the Post Falls monitoring period.

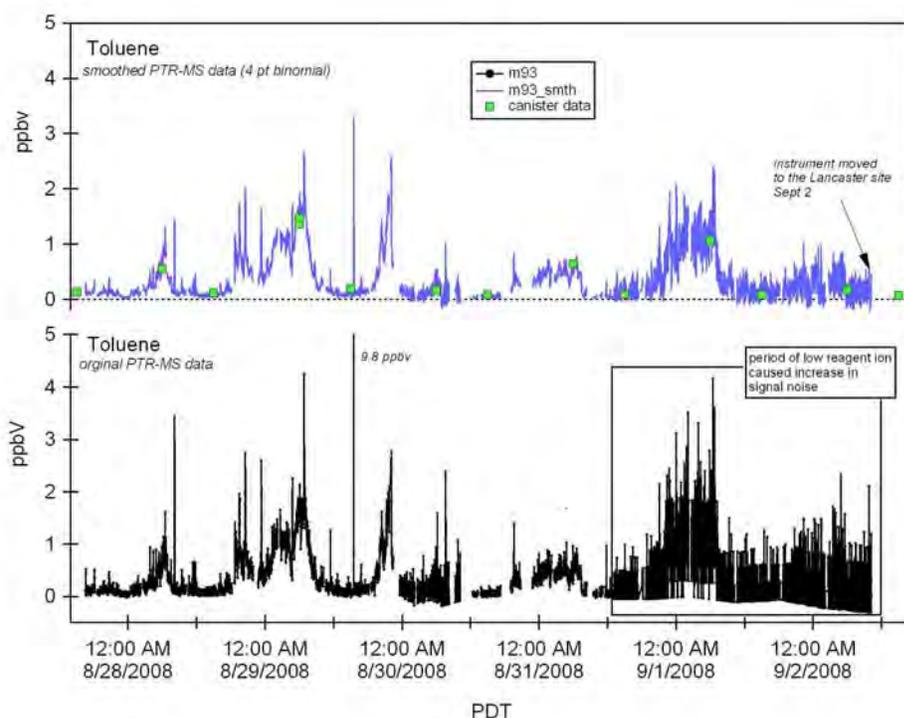


Figure 2. Toluene data from PTR-MS at Post Falls illustrating change in signal to noise when reagent ion counts rates fell to 2×10^5 Hz during the last several days. Lower panel shows original toluene data. Upper panel has been smoothed using a 4 point binomial smoothing algorithm.

The PTR-MS data was smoothed (4 point binomial smooth) to reveal temporal trends within the noise. The smoothed data are shown in the upper panel of Figure 2. For several species (styrene, C₃-benzenes) the signal to noise during this period was too poor and the data were below the instrument detection limit.

The CO instrument suffers from temperature dependent background signal level. By monitoring the interior shelter temperature with our data system we were able to account for background drift changes due to instrument temperature changes.

Canister analysis by GC-MS was not performed as planned due to calibration issues using our multicomponent standard. The sensitivities for individual compounds did not match past records and yielded highly variable results. This problem could not be resolved and the canisters were therefore re-analyzed on a different GC system using flame ionization as detection. The canisters were thus analyzed for C₂-C₆ hydrocarbons by GC-FID on an Al₂O₃/KCl column as originally planned, and for C₆-C₁₀ hydrocarbons by GC-FID on an HP-624 column (the same column used in the GC-MS analysis). The carbon response of both GC-FID systems was determined from a NIST traceable standard of 2,2-dimethylbutane. Compound identification was based on retention times which were determined from multicomponent gas standards. Peak identity using the HP-624 column in the GC-FID system was verified by GC-MS analysis using the same HP-624 column and chromatographic conditions.

3. OBSERVATIONS

3.1 Criteria Pollutants

There was no evidence of elevated ozone mixing ratios that could be attributed to photochemical pollution during the study. Ozone mixing ratios ranged from a low of 0 ppbv to a typical regional background value of ~ 45 ppbv. During the evening and early morning ozone was often low due to reaction with NO to form NO₂.

NO_x mixing ratios were on average higher at Post Falls than at Lancaster and displayed more variability. However the Lancaster site experienced three periods where NO_x mixing ratios were significantly elevated (> 40 ppbv) compared to the typical average mixing ratio of 3 ppbv at the site, suggesting the impact of a point source plume. Peak mixing ratios for these events occurred in the morning between 6 and 7 am on Sept 3, Sept 5 and Sept 9. These events also had elevated levels of CO (~260 ppbv)

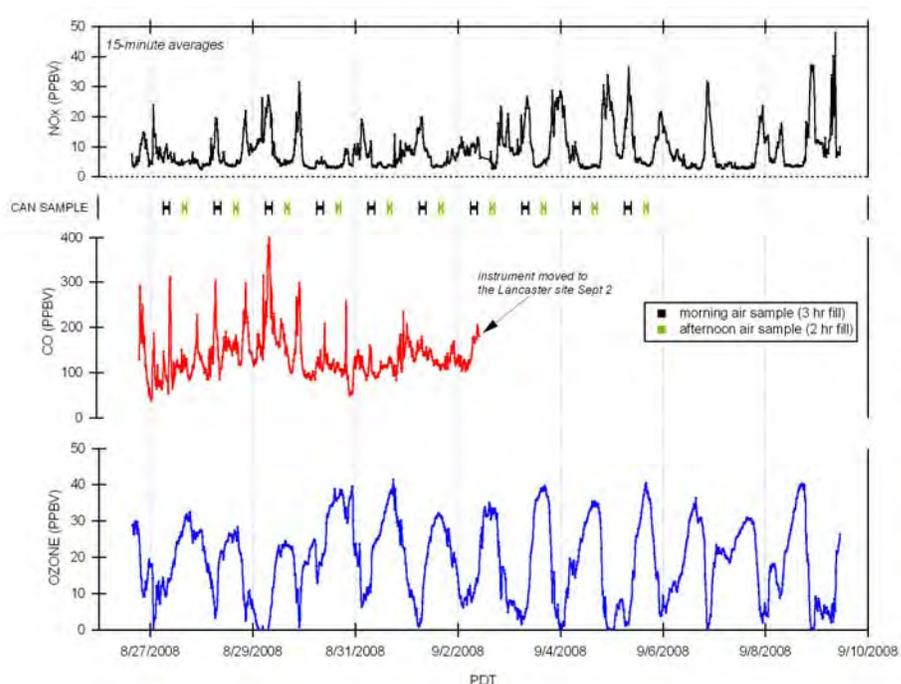


Figure 3.1.1 Post Falls data showing NO_x, CO, and O₃ mixing ratios and can sampling times.

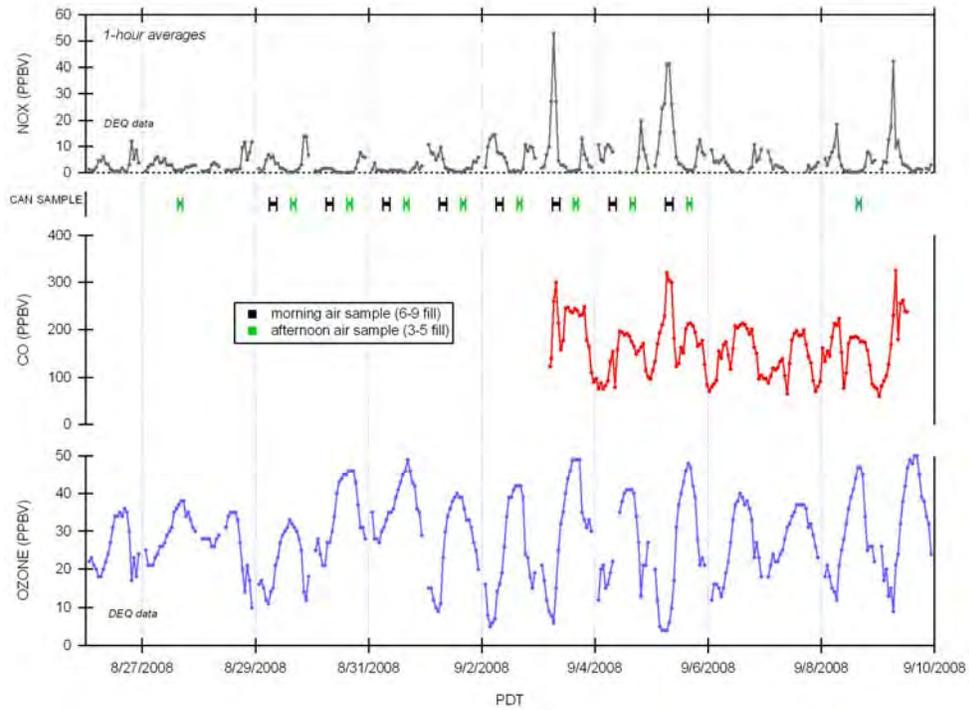


Figure 3.1.2 Lancaster data showing NO_x, CO, and O₃ mixing ratios and can sampling times.

3.2 PTR-MS Volatile Organic Compound Data

The following figures show time series of organic compounds measured by the PTR-MS. The displayed data are 4 point binomial smoothed to improve signal-to-noise.

Aromatic Species

Aromatic species are a good general indicator of vehicle exhaust. Aromatic species mixing ratios were typically largest during the evening and morning when vehicle emissions are contained within shallow mixed layers. A couple of short term “spikes” of elevated toluene mixing ratios were observed at Post Falls and Lancaster indicating local sources, perhaps use of toluene based solvents or paints.

Oxygenated Species

On average oxygenated species were the most abundant VOCs measured at Post Falls and Lancaster. Methanol was the most abundant VOC measured with mixing ratios ranging from 2 to 12 ppbv.

At the Post Falls site on August 28 at ~ 19:30 there were elevated levels of acetone (max = 9.5 ppbv), methanol (max 11.5 ppbv), and 2-butanone (max = 0.9 ppbv) for ~ ½ hr period suggesting a local source, perhaps solvent use.

At the Lancaster site there were two periods of elevated levels of 2-butanone (Sept 3 and Sept 9) that were associated with elevated levels of toluene, again suggesting local solvent use.

Biogenic Species

Monoterpenes were more abundant than isoprene and displayed very elevated mixing ratios during the night at the Lancaster site, where total monoterpene mixings ratios as high as 12 ppbv were observed. Canister data showed both α -pinene and β -pinene were present. Significant levels of the β -pinene + O₃ oxidation product nopinone were measured, indicating active chemistry that can lead to secondary organic aerosol production. It is not unusual to see elevated terpene levels during nighttime conditions since vegetation emits terpenes continuously primarily as a function of temperature and these emissions are contained with a very shallow surface boundary layer.

Tracer Species

Elevated levels of styrene were observed on only one occasion during the entire study. This occurred at Post Falls on August 31 between 6 and 7 am with mixing ratios maximizing at ~ 1.4 ppbv. This plume may be associated with emissions from Foam Molders, a company located to the NW on highway 53. There was no evidence at either site being impacted by smoke during the study as indicated by low and invariant acetonitrile mixing ratios (average = 80 pptv). Naphthalene mixing ratios were also low and invariant. Naphthalene was proposed in this study as a tracer for local asphalt operations.

3.2.1 Aromatic Species

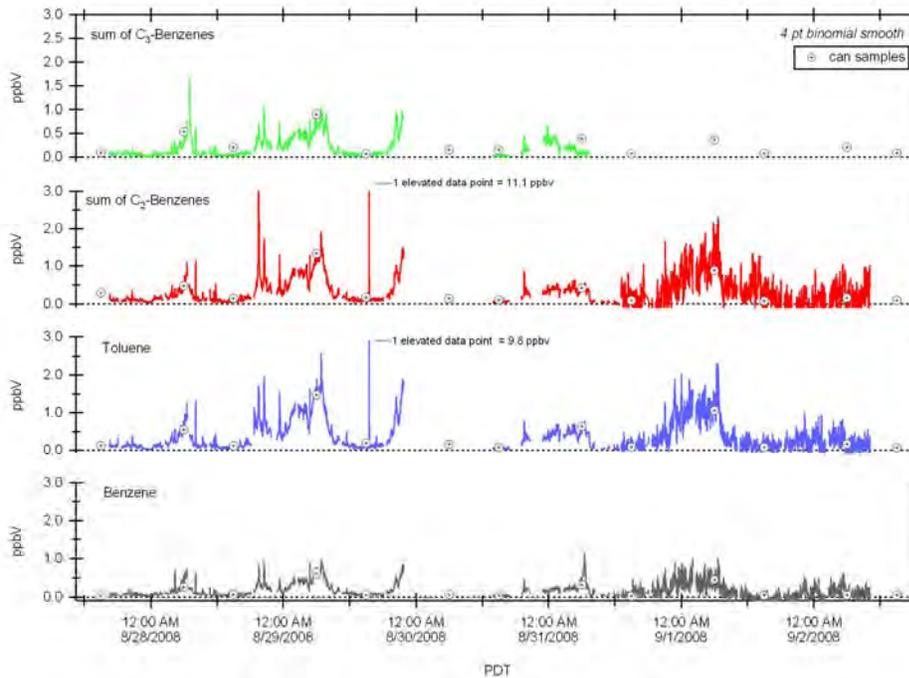


Figure 3.2.1a Post Falls PTR-MS data (lines) and canister data (circles).

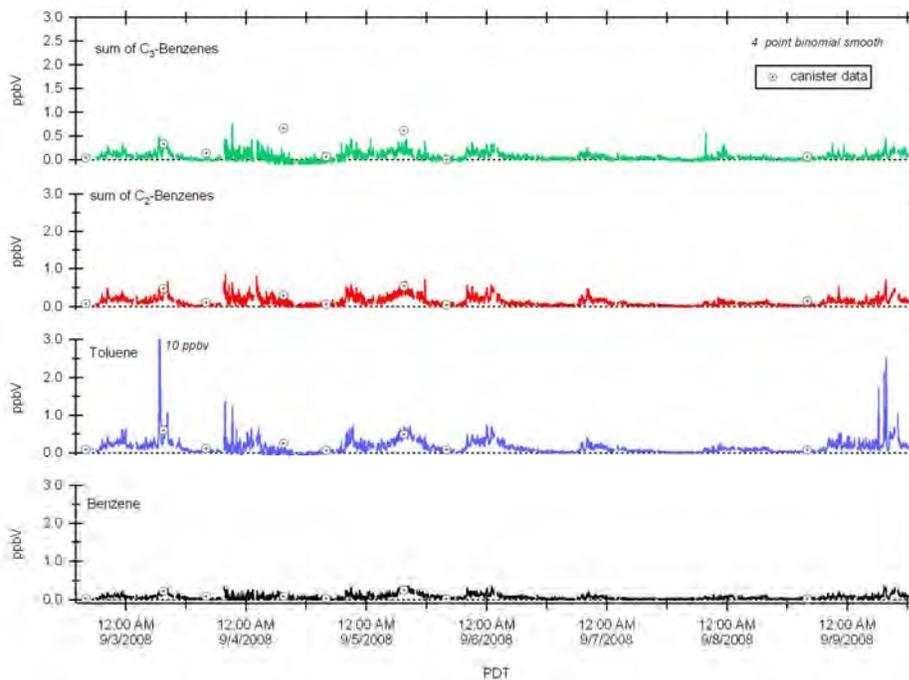


Figure 3.2.1b Lancaster PTR-MS data (lines) and canister data (circles).

3.2.2 Oxygenated Species

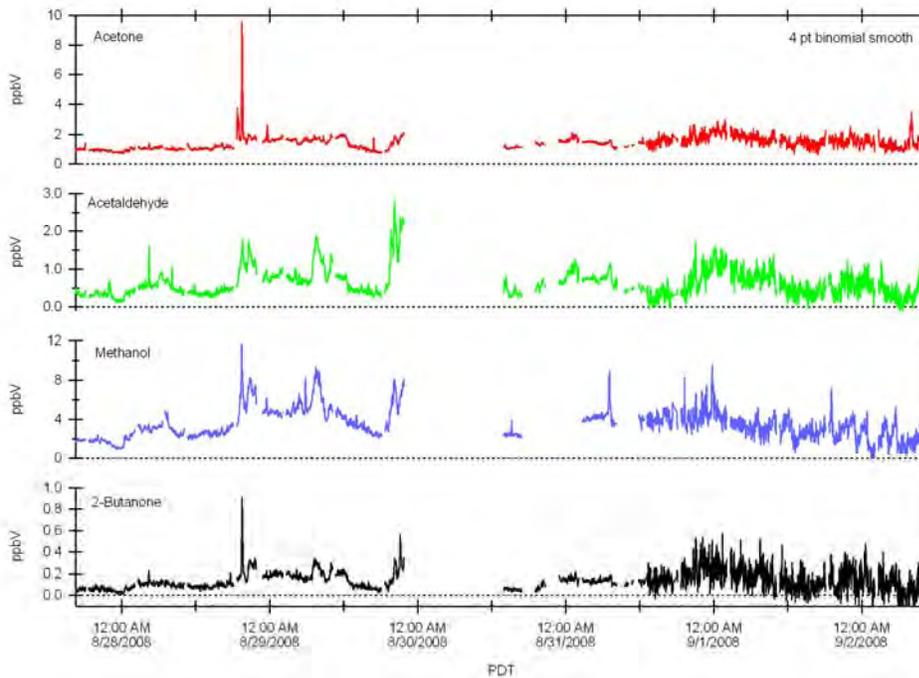


Figure 3.2.2a Post Falls PTR-MS data (lines) and canister data (circles).

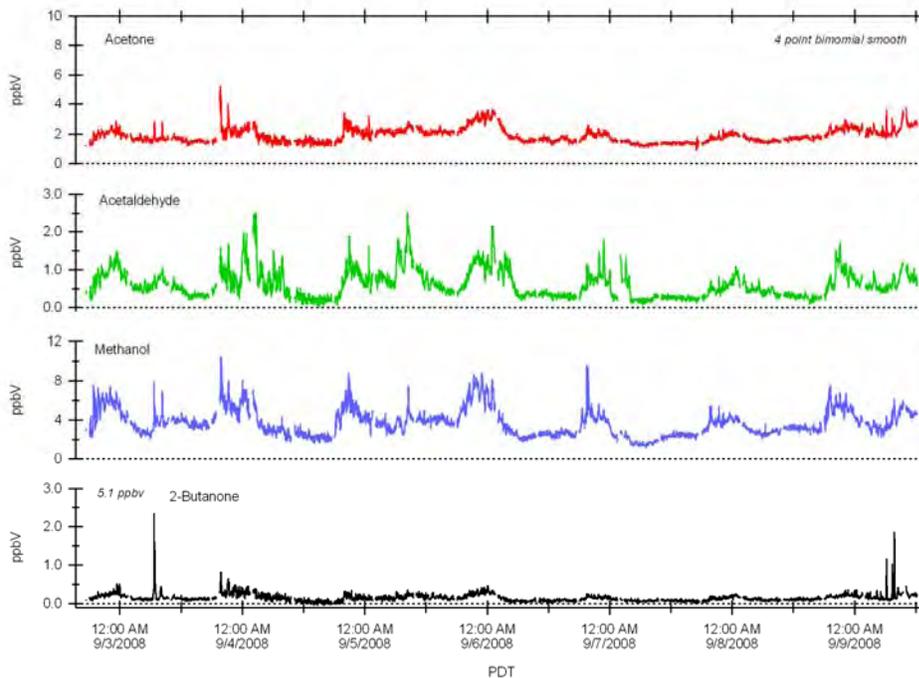


Figure 3.2.2b Lancaster PTR-MS data (lines) and canister data (circles).

3.2.3 Biogenic Hydrocarbons and their Oxidation Products

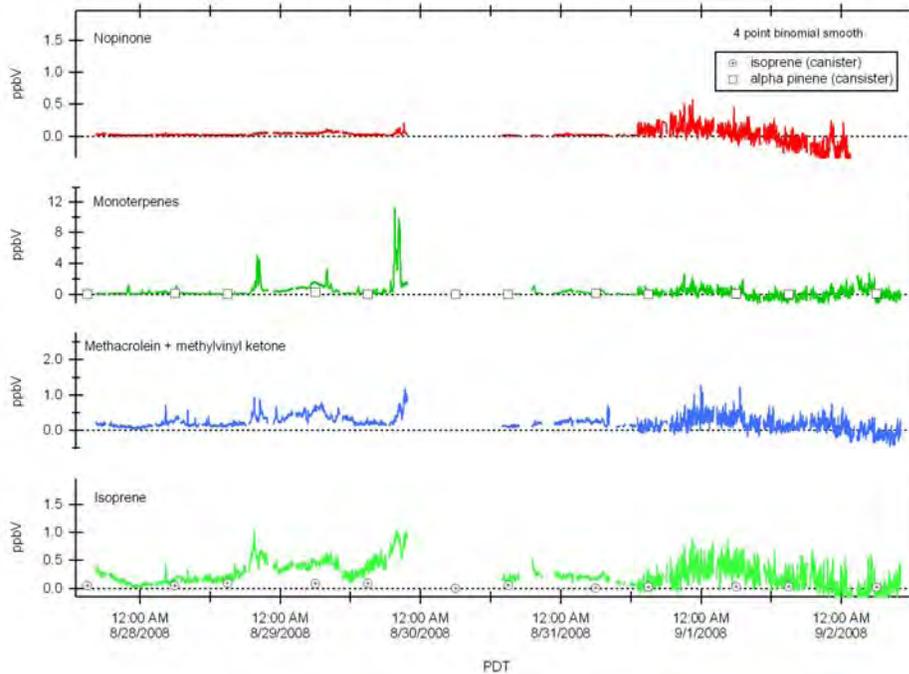


Figure 3.2.3a Post Falls PTR-MS data (lines) and canister data (circles).

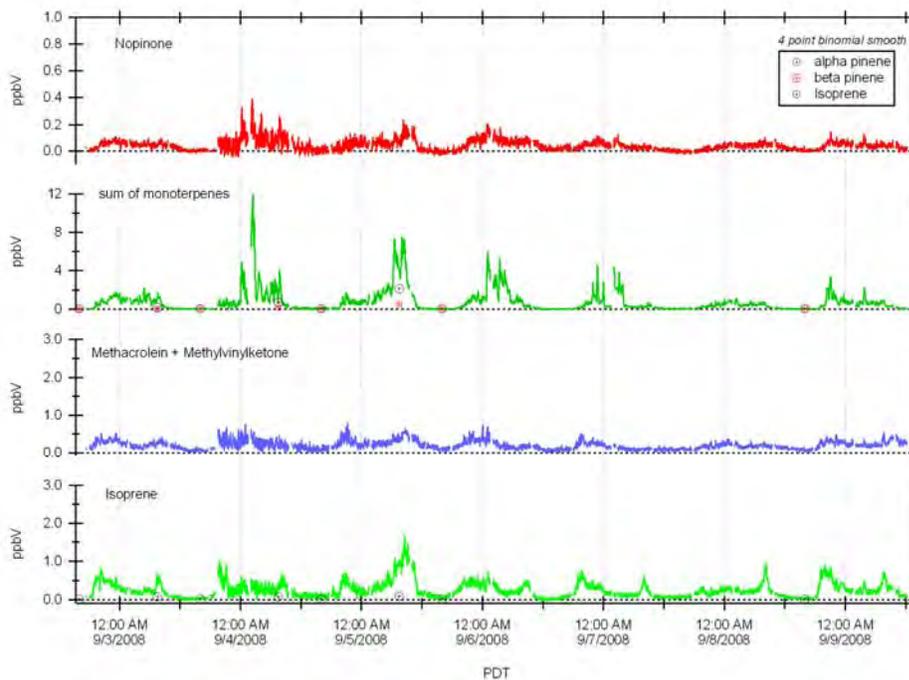


Figure 3.2.3b Lancaster PTR-MS data (lines) and canister data (circles).

3.2.4 Selected Tracer Compounds

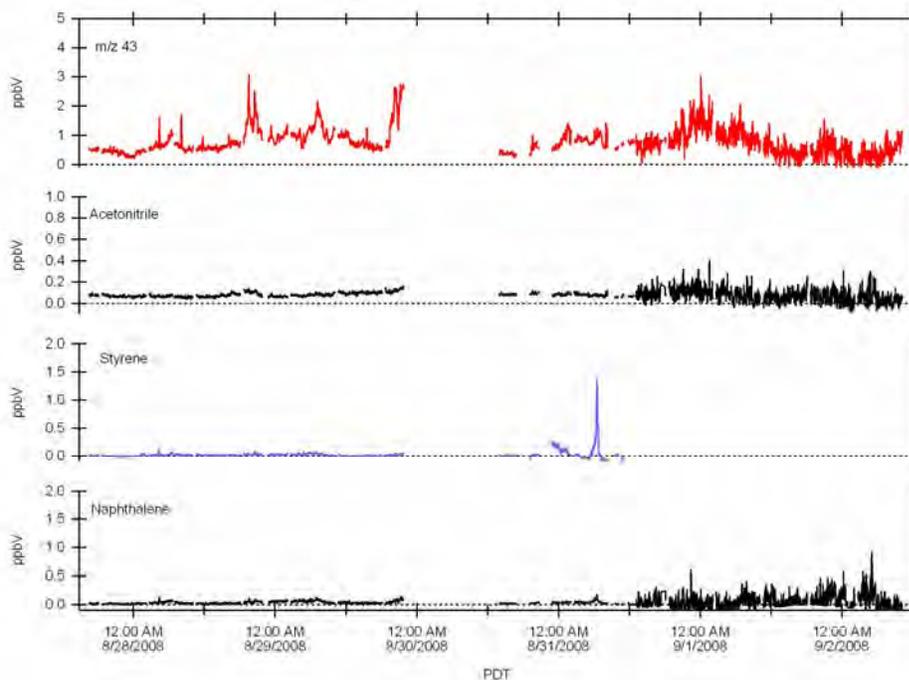


Figure 3.2.4a Post Falls PTR-MS data (lines) and canister data (circles).

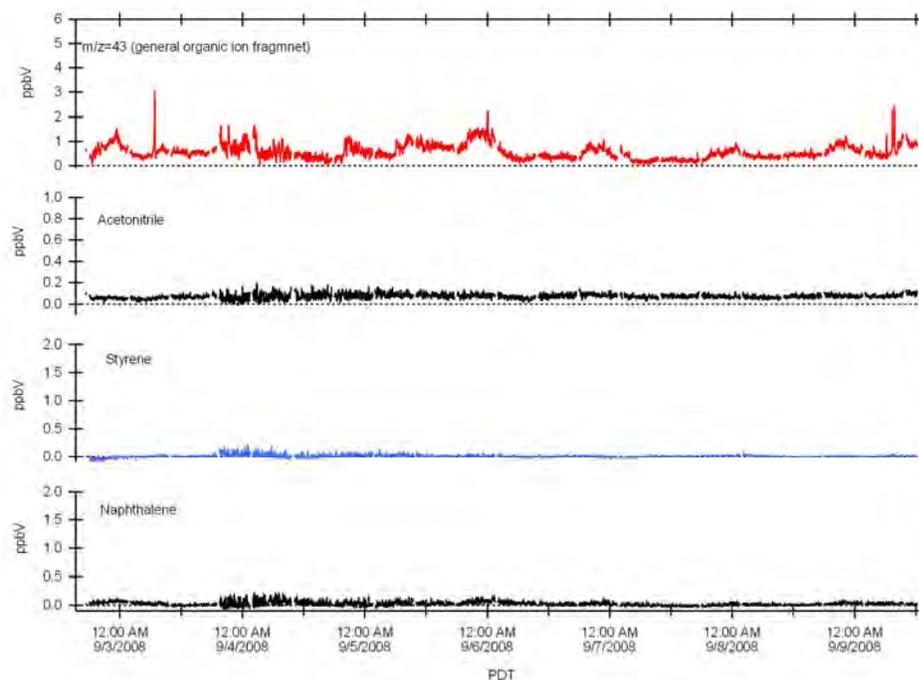


Figure 3.2.4b Lancaster PTR-MS data (lines) and canister data (circles).

3.3 Canister Data

The average, maximum, and minimum mixing ratios of species determined from morning samples and afternoon samples are given in Tables 4 for Post Falls and Table 5 for Lancaster. The average mixing ratios determined for the AM and PM samples are compared for each site in Figures 3.3.1 and 3.3.2. An estimate of the total amount of VOC in the morning canister samples was determined from the sum of the peak areas from GC-FID analysis using the HP-624 column analysis. This value will include most VOCs from C₂-C₁₂ including some oxygenated species such as methanol, acetaldehyde, and acetone. The value is given in units of ppbC.

On average, afternoon mixing ratios of hydrocarbons at Post Falls were a factor of 3.9 lower than the morning average. At Lancaster, the afternoon mixing ratios were on average a factor of 3.5 less than morning values, very similar to Post Falls. Notable exceptions at the Lancaster site were the monoterpenes. α -Pinene was factor of 18 higher in the morning and β -pinene was a factor of 17 higher.

The relative abundance of the hydrocarbons with respect to *i*-pentane for the morning samples are shown in Figures 3.3.3 and 3.3.4. These ratios are compared to a reference data set collected from downtown Los Angeles in October 2006. The Los Angeles data is used as a reference hydrocarbon distribution for roadway autoexhaust. *i*-Pentane is a major constituent of gasoline and one of the dominant hydrocarbons emitted in vehicle exhaust. Despite large differences in mixing ratios between Post Falls and Los Angeles, the relative amounts of hydrocarbons with respect to *i*-pentane are very similar. This suggests that vehicle emissions are the major source of hydrocarbons observed at Post Falls. The Lancaster hydrocarbon distribution is also very similar to the LA pattern. The most significant differences at Lancaster are the larger amounts of biogenic hydrocarbons (α -pinene and β -pinene) at Lancaster and the lower relative abundance of reactive aromatic compounds compared to LA. The lower abundance of aromatics would be consistent with more chemically processed air as would be anticipated from a rural site.

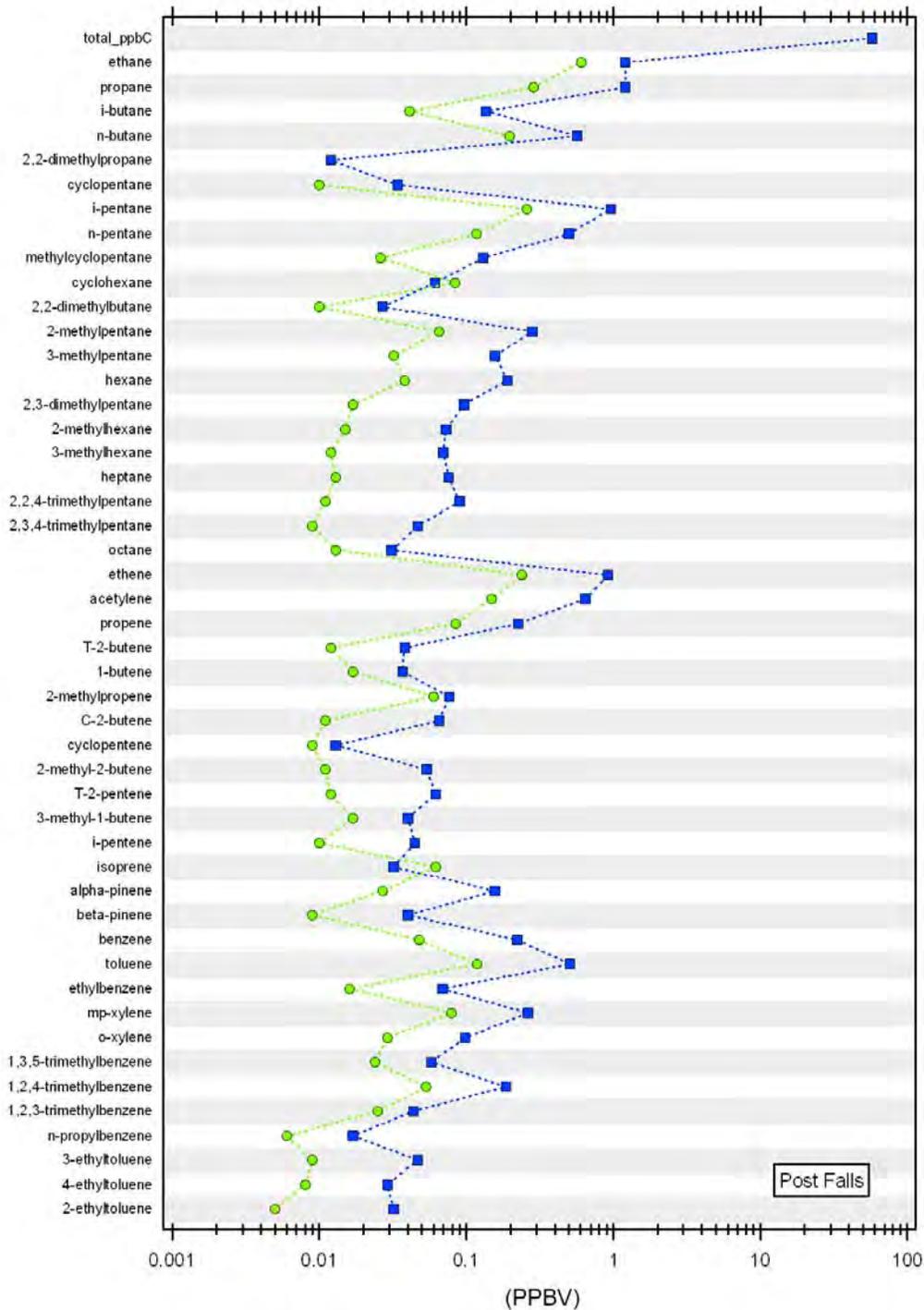


Figure 3.3.1 Average mixing ratios determined at Post Falls for morning canisters (squares) and afternoon canisters (circles).

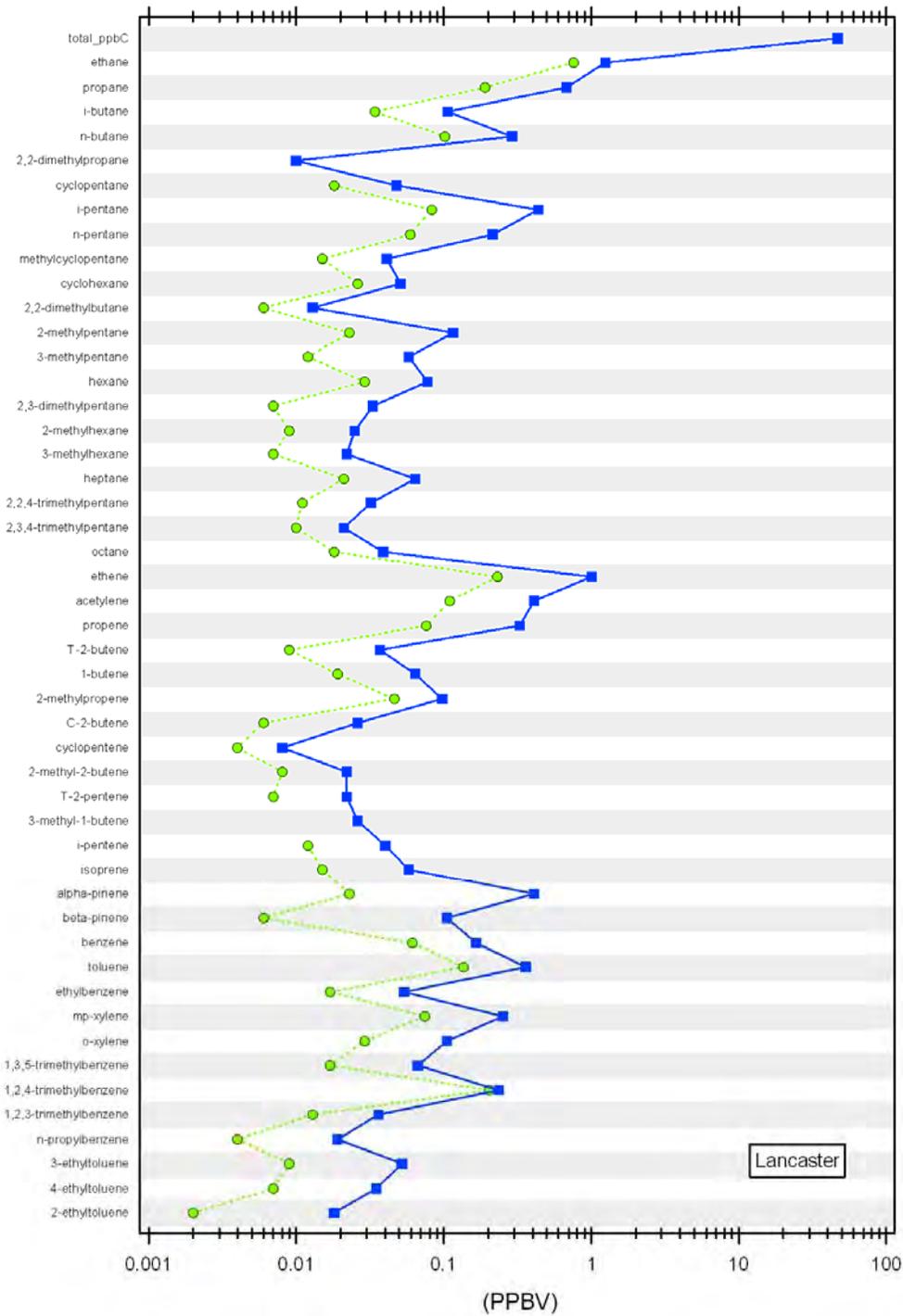


Figure 3.3.2 Average mixing ratios determined at Lancaster for morning canisters (squares) and afternoon canisters (circles).

Table 4. Post Falls Hydrocarbon Mixing Ratios (ppbv)

Species	Morning 6-9 AM			Afternoon 3-5 PM		
	Average	Max	Min	Average	Max	Min
Alkanes						
Ethane	1.213	2.065	0.710	0.605	0.720	0.359
Propane	1.212	2.780	0.265	0.287	0.547	0.169
i-butane	0.136	0.399	0.041	0.041	0.065	0.027
n-butane	0.566	1.645	0.171	0.196	0.369	0.108
2,2-dimethylpropane	0.012	0.086	< DL	< DL	0.005	< DL
Cyclopentane	0.034	0.120	< DL	0.010	0.020	< DL
i-pentane	0.957	2.875	0.169	0.258	0.485	0.146
n-pentane	0.496	1.517	0.021	0.117	0.212	0.069
methylcyclopentane	0.131	0.455	0.038	0.026	0.041	0.017
Cyclohexane	0.061	0.133	0.034	0.084	0.493	0.028
2,2-dimethylbutane	0.027	0.078	0.008	0.010	0.026	0.005
2-methylpentane	0.281	0.944	0.072	0.065	0.095	0.042
3-methylpentane	0.156	0.470	0.044	0.032	0.047	0.020
Hexane	0.191	0.571	0.058	0.038	0.057	0.025
2,3-dimethylpentane	0.096	0.256	0.029	0.017	0.025	0.008
2-methylhexane	0.073	0.193	0.023	0.015	0.022	0.008
3-methylhexane	0.070	0.200	0.021	0.012	0.018	0.007
Heptane	0.076	0.194	0.018	0.013	0.022	0.006
2,2,4-trimethylpentane	0.090	0.262	0.012	0.011	0.015	0.007
2,3,4-trimethylpentane	0.047	0.138	0.007	0.009	0.012	0.006
Octane	0.031	0.077	0.009	0.013	0.022	0.007
Alkenes & Alkynes						
Ethene	0.924	1.941	0.241	0.239	0.391	0.179
Acetylene	0.642	1.269	0.216	0.149	0.201	0.110
Propene	0.226	0.530	0.051	0.085	0.158	0.050
T-2-butene	0.038	0.148	0.007	0.012	0.026	0.007
1-butene	0.037	0.096	0.010	0.017	0.042	0.008
2-methylpropene	0.077	0.253	0.014	0.060	0.197	0.033
C-2-butene	0.065	0.381	0.007	0.011	0.021	0.005
Cyclopentene	0.013	0.054	0.000	0.009	0.020	0.000
2-methyl-2-butene	0.054	0.261	0.000	0.011	0.019	0.005
T-2-pentene	0.062	0.310	0.005	0.012	0.025	0.004
3-methyl-1-butene	0.040	0.104	0.011	0.017	0.035	0.008
1-pentene	0.045	0.168	0.009	0.010	0.021	< DL

Isoprene	0.032	0.090	0.006	0.062	0.100	0.031
α -pinene	0.156	0.416	0.037	0.027	0.043	0.011
β -pinene	0.040	0.118	0.008	0.009	0.016	0.000
Aromatics						
Benzene	0.222	0.612	0.047	0.048	0.079	0.020
Toluene	0.510	1.473	0.155	0.118	0.198	0.075
Ethylbenzene	0.069	0.208	0.021	0.016	0.028	0.007
m,p-xylene	0.263	0.825	0.068	0.079	0.170	0.030
o-xylene	0.098	0.301	0.028	0.029	0.089	0.011
1,3,5-trimethylbenzene	0.058	0.159	0.014	0.024	0.041	0.015
1,2,4-trimethylbenzene	0.186	0.500	0.054	0.053	0.110	0.027
1,2,3-trimethylbenzene	0.044	0.080	0.025	0.025	0.043	0.008
n-propylbenzene	0.017	0.038	0.005	0.006	0.018	< DL
3-ethyltoluene	0.047	0.150	0.012	0.009	0.026	< DL
4-ethyltoluene	0.029	0.072	0.009	0.008	0.019	< DL
2-ethyltoluene	0.032	0.099	0.008	0.005	0.019	< DL

< DL = below detection limit

Table 5. Lancaster Hydrocarbon Mixing Ratios (ppbv)

Species	Morning 6-9 AM			Afternoon 3-5 PM		
	Average	Max	Min	Average	Max	Min
Alkanes						
Ethane	1.251	3.886	0.639	0.760	1.451	0.528
Propane	0.683	1.239	0.194	0.191	0.400	0.011
i-butane	0.106	0.352	0.022	0.034	0.059	0.015
n-butane	0.289	1.004	0.083	0.102	0.268	0.045
2,2-dimethylpropane	0.010	0.060	< DL	< DL	0.004	< DL
cyclopentane	0.048	0.259	< DL	0.018	0.121	< DL
i-pentane	0.439	1.169	0.114	0.083	0.133	0.034
n-pentane	0.215	0.498	0.061	0.059	0.147	0.027
methylcyclopentane	0.041	0.095	0.016	0.015	0.030	0.007
cyclohexane	0.051	0.122	0.029	0.026	0.031	0.003
2,2-dimethylbutane	0.013	0.025	0.004	0.006	0.013	0.000
2-methylpentane	0.116	0.232	0.031	0.023	0.044	0.012
3-methylpentane	0.058	0.117	0.019	0.012	0.027	0.005
Hexane	0.078	0.150	0.024	0.029	0.083	0.006
2,3-dimethylpentane	0.033	0.064	0.007	0.007	0.016	0.004
2-methylhexane	0.025	0.051	0.006	0.009	0.025	0.004
3-methylhexane	0.022	0.052	0.005	0.007	0.014	0.003
Heptane	0.064	0.162	0.026	0.021	0.058	0.009
2,2,4-trimethylpentane	0.032	0.083	0.010	0.011	0.028	0.004
2,3,4-trimethylpentane	0.021	0.053	0.006	0.010	0.024	0.005
Octane	0.039	0.093	0.010	0.018	0.036	0.006
Alkenes & Alkynes						
Ethene	1.002	1.883	0.303	0.232	0.436	0.134
acetylene	0.410	0.984	0.141	0.110	0.177	0.015
Propene	0.328	0.592	0.080	0.076	0.196	0.031
T-2-butene	0.037	0.113	0.008	0.009	0.018	0.005
1-butene	0.064	0.129	0.023	0.019	0.037	0.008
2-methylpropene	0.097	0.266	0.011	0.046	0.096	0.020
C-2-butene	0.026	0.097	< DL	0.006	0.013	< DL
cyclopentene	0.008	0.015	< DL	0.004	0.006	< DL
2-methyl-2-butene	0.022	0.040	0.006	0.008	0.038	0.004
T-2-pentene	0.022	0.062	0.009	0.007	0.024	0.004
3-methyl-1-butene	0.026	0.049	0.008	0.010	0.026	0.005
1-pentene	0.040	0.081	0.015	0.012	0.031	0.004

isoprene	0.058	0.097	0.026	0.015	0.036	0.007
α -pinene	0.412	2.103	< DL	0.023	0.053	0.010
β -pinene	0.105	0.498	< DL	0.006	0.013	< DL
Aromatics						
Benzene	0.165	0.285	0.060	0.061	0.152	0.018
Toluene	0.361	0.643	0.107	0.136	0.382	0.066
ethylbenzene	0.054	0.097	0.015	0.017	0.035	0.006
mp-xylene	0.251	0.432	0.074	0.074	0.134	0.020
o-xylene	0.105	0.171	0.042	0.029	0.046	0.011
1,3,5-trimethylbenzene	0.067	0.160	0.021	0.017	0.038	< DL
1,2,4-trimethylbenzene	0.524	2.349	0.083	0.202	0.989	< DL
1,2,3-trimethylbenzene	0.036	0.077	< DL	0.013	0.040	< DL
n-propylbenzene	0.019	0.039	< DL	0.004	0.014	< DL
3-ethyltoluene	0.052	0.121	< DL	0.009	0.034	< DL
4-ethyltoluene	0.035	0.093	< DL	0.007	0.027	< DL
2-ethyltoluene	0.018	0.051	< DL	< DL	0.015	< DL

< DL = below detection limit

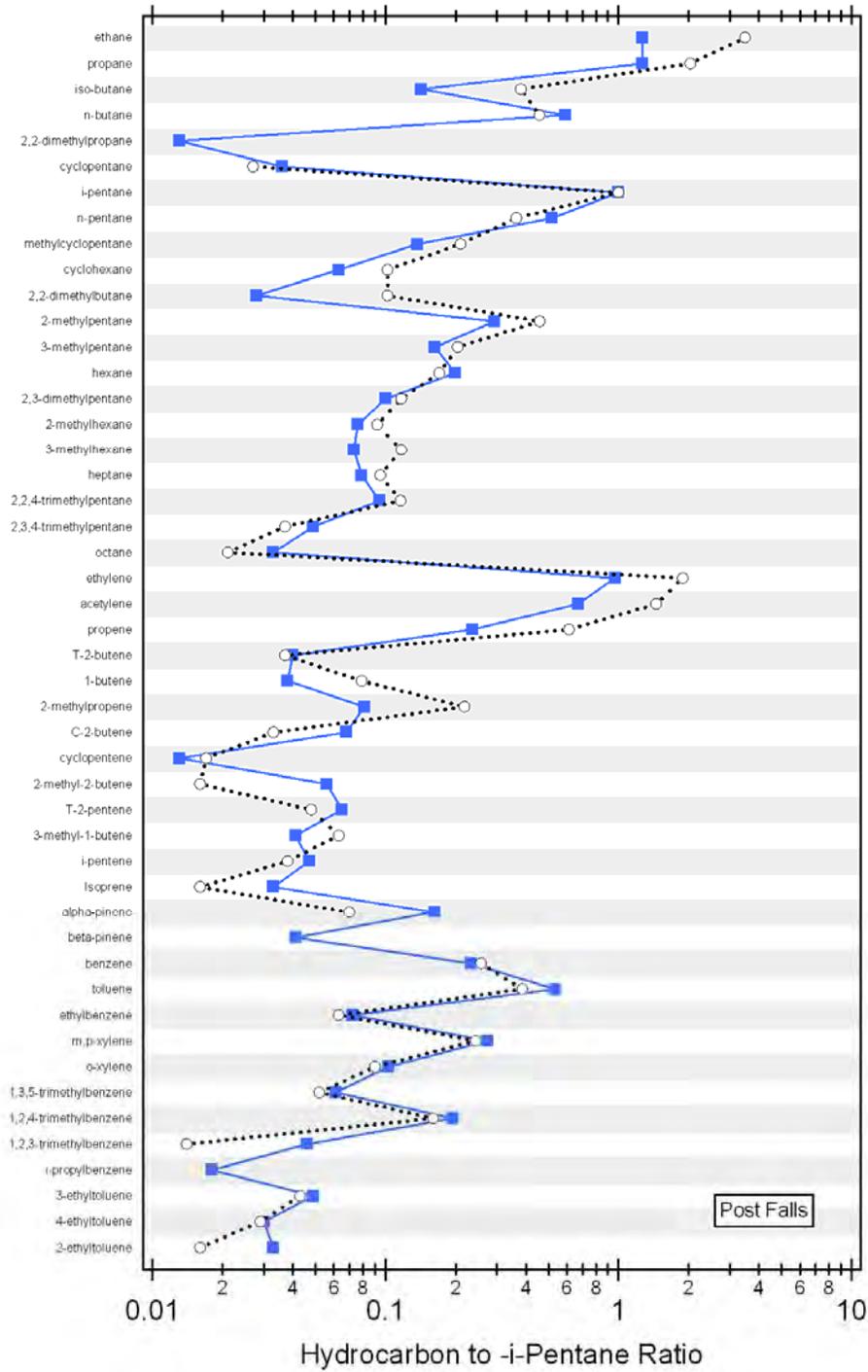


Figure 3.3.3. Post Falls data solid blue squares, down town Los Angeles data open circles.

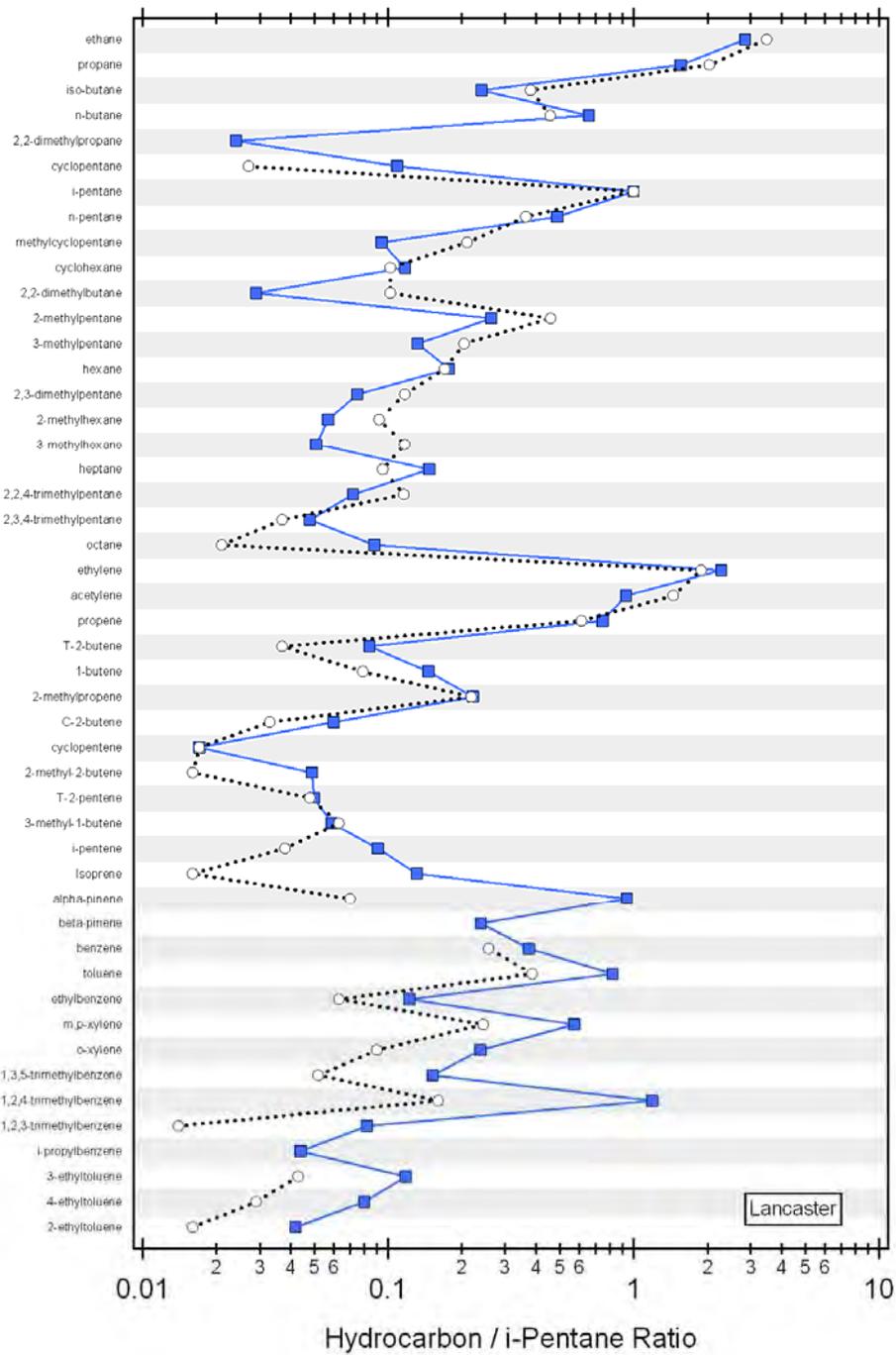


Figure 3.3.4. Lancaster data solid blue squares, downtown Los Angeles data open circles.

4. ANALYSIS & RESULTS

4.1 VOC / NO_x ratios

The VOC / NO_x ratio is used to indicate the limiting chemical reagents in ozone formation. The use of the ratio stems from smog chamber and modeling studies. Such studies have shown that ozone production and maximum concentration is a non-linear function of the concentration of VOCs and NO_x. The VOC / NO_x ratio is an indicator of whether ozone production is limited by the concentration of VOCs or NO_x. Low ratios indicate ozone production is limited by VOC concentrations. High ratios indicate ozone production is limited by NO_x concentrations.

To better understand the use of the ratio it is important to understand the underlying chemistry that produces ozone. The production of ozone is initiated by the oxidation of organic compounds (RH) by the hydroxyl radical (OH). In the presence of air this reaction forms a reactive organic peroxy radical (RO₂). As an example reaction OH can remove a hydrogen atom from an organic compound to form water.



The RO₂ radical oxidizes NO to NO₂ and the RO radical is formed as a product. NO₂ rapidly photolyzes in the presence of sunlight (*hν*) to form O₃.



The RO radical produced in R2 can react with O₂ to form a carbonyl compound (R'CHO) and hydroperoxy radical (HO₂). This radical can also oxidize NO to NO₂, leading to formation of another ozone molecule. Note that the OH radical is reformed in the process.



The carbonyl compound is a photoproduct (secondary VOC) and can react with OH to start another oxidation cycle.

During the day the ozone production rate (P) is limited by the rate of NO oxidation by RO₂ and HO₂ since NO₂ photolysis (R3) is very rapid. The ozone production rate is given by the equation

$$P = k_2[\text{RO}_2][\text{NO}] + k_6[\text{HO}_2][\text{NO}] \quad (1)$$

where *k*₂ and *k*₆ are the bimolecular rate coefficients for reactions R2 and R6. Equation (1) shows that the rate of ozone formation depends on NO concentration and the concentrations of RO₂ and HO₂ radicals formed in the OH initiated oxidation of VOC. The resulting ozone

concentration depends on this rate and meteorological conditions such as mixed layer heights and dispersion rates.

At low NO_x concentrations P is limited by the concentration of NO and the photochemical system is said to be NO_x limited. At high NO_x concentrations NO₂ competes with VOCs for OH radicals. The reaction of OH with NO₂ to form nitric acid (HNO₃) reduces OH radical concentrations, therefore reducing the formation rates of RO₂ and HO₂.



In this situation the photochemical system is said to be VOC limited. More VOCs would increase the rate of (R1) and increase the concentration of RO₂ and HO₂ radicals.

The types of VOC present also impact ozone formation rates. VOCs that react rapidly with OH will lead to rapid local production of RO₂ and HO₂. The complex chemistry of RO₂ and RO radicals, not discussed here for simplicity, also determines how efficient a VOC will be in producing O₃. The types of VOC and how reactive they are towards OH is an important variable in ozone formation. The VOC / NO_x ratio analysis developed from chamber studies typically used an urban VOC mix which is dominated by organics emitted in vehicle exhaust. Typically VOC / NO_x ratios are determined for the morning rush hour. This is the mixture that will be reacting over the course of the day to produce ozone. In rural areas the VOC mixture will be dominated by biogenic emissions and the VOC / NO_x ratio values that define NO_x limitation or VOC limitation may be different from urban areas.

There is no standard method for calculating VOC to NO_x ratios from ambient data. This is because of the wide variety of methods used to measure VOCs and that no one method measures all the VOCs present in air. For example many methods based on canister sample and collection are not suited for determining oxygenated VOCs such as methanol, formaldehyde, and acetaldehyde. The most practical approach is to determine the total peak area in a GC-FID chromatogram and report the total carbon present in the sample in units of ppbC. This unit follows from use of the flame ionization detector (FID) which responds equally to carbon atoms bonded to hydrogen atoms from all types of organic compounds. The unit ppbC (parts per billion by carbon) and ppbv are related by:

$$\text{ppbC} = \text{ppbv} * (\text{number carbon atoms in molecule})$$

For this study the VOC to NO_x ratios were calculated by averaging the NO_x data over the morning canister fill times and using the total VOC concentration determined from GC-FID analysis on the HP-624 column. VOC / NO_x ratios at Post Falls are shown in Table 6. The ratios ranged from a low of 2.6 to a high of 11 ppbC / ppbv. The last 5 days of sampling at Post Falls, from Sept 2 to Sept 9, displayed very similar VOC / NO_x ratios of 2.7 ppbC / ppbv. These are reasonably low values and suggest that ozone production chemistry is VOC limited.

The morning Lancaster data generally displayed larger VOC / NO_x ratios than Post Falls. Table 7 shows the VOC / NO_x ratio ranged from 2.2 to 31 ppbC / ppbv at Lancaster. The larger ratios

occurred during low NO_x concentrations and are not representative of polluted conditions that could lead to ozone production. For the days with the highest NO_x concentrations during canister sampling, 21.9 ppbv on Sept 3 and 31 ppbv on Sept 5, the corresponding VOC / NO_x ratios were 2.2 and 2.7 ppbv / ppbv. These values are very similar to the Post Falls data from the same period and suggest the site is VOC limited.

Table 6. Post Falls: Average Mixing Ratios during Morning Canister Fill Time

Day	Avg. NO _x (ppbv)	Avg. CO (ppbv)	Total VOC (ppbC)	VOC / NO _x (ppbC / ppbv)
8/27	7.8	113	31	4.0
8/28	12.2	172	53	4.3
8/29	22.4	300	154	6.9
8/30	4.9	119	16	3.3
8/31	6.3	117	67	11
9/1	14.2	157	116	8.2
9/2	10.1	166	28	2.8
9/3	19.8		53	2.7
9/4	7.1		20	2.8
9/5	24.1		67	2.8
9/8	11.7		31	2.6

Table 7. Lancaster: Average Mixing Ratio during Morning Canister Fill Time

Day	Avg. NO _x (ppbv)	Avg. CO (ppbv)	Total VOC (ppbC)	VOC / NO _x (ppbC / ppbv)
8/29	4.8		98	20
8/30	1.3		23	17
8/31	0.7		22	31
9/1	4.5		28	6.2
9/2	7.1		39	5.5
9/3	21.9	232	47	2.2
9/4	8.8	130	34	3.9
9/5	31.0	276	85	2.7

4.2 Hydrocarbon Reactivity

The VOCs driving ozone formation can be ranked based on their reaction rate with OH (R1). This is found by multiplying the measured VOC concentration by the corresponding OH rate coefficient. The product has units of s^{-1} and is often called the hydrocarbon reactivity or more precisely the OH loss frequency. The inverse of the sum of the individual loss frequencies yields the OH lifetime due to reaction with VOCs. Tables 8 and 9 show the 5 species with the largest OH loss frequencies for Post Falls and Lancaster AM and PM canister samples. Data from the PTR-MS have been averaged over the same time interval. The PTR-MS data contains values for oxygenated species that are not measured in the canister samples. The PTR-MS is not able to distinguish between the isoprene oxidation products methacrolein (MACR) and methylvinylketone (MVK) and so their sum is reported. Their average OH rate coefficient was used to estimate the OH loss frequency due to these compounds.

Table 8. Post Falls OH Loss Frequencies

AM species	AM OH loss frequency (Hz)	PM Species	PM OH loss frequency (Hz)
acetaldehyde	0.284	isoprene	0.156
α -pinene	0.210	acetaldehyde	0.147
ethene	0.197	MVK + MACR	0.098
1,2,4-trimethylbenzene	0.151	methanol	0.069
propene	0.148	propene	0.056

Table 9. Lancaster OH Loss Frequencies

AM species	AM OH loss frequency (Hz)	PM Species	PM OH loss frequency (Hz)
α -pinene	0.553	1,2,4-trimethylbenzene	0.164
1,2,4-trimethylbenzene	0.426	acetaldehyde	0.109
acetaldehyde	0.382	methanol	0.069
propene	0.216	isobutylene	0.060
ethene	0.213	MVK + MACR	0.058

The tables show the importance of the biogenic compound α -pinene and the oxygenated compound acetaldehyde in the morning for both the Post Falls and Lancaster sites. Light alkenes and reactive aromatics emitted from vehicle exhaust were also important as to be expected. The total OH loss frequency for the AM Post Falls samples was $2.82 s^{-1}$ and for Lancaster it was $3.45 s^{-1}$.

In the afternoon isoprene chemistry dominates the Post Falls site. Isoprene and its oxidation products MVK and MACR, and the oxygenated compounds methanol and acetaldehyde were the most important reactive VOC species. At Lancaster the aromatic compound 1,2,4-trimethylbenzene was most important species. The oxygenated species acetaldehyde, methanol, and MVK+MACR were also important. The total OH loss frequency for the PM Post Falls samples was $1.13 s^{-1}$ and for Lancaster it was $0.91 s^{-1}$.

4.2 High NO_x Events at Lancaster.

Figure 4.2.1 shows a timeseries of NO_x mixing ratios illustrating the 3 “events” where NO_x mixing ratios > 30 ppbv. What is evident from the figure is that these events occurred during early morning hours when wind speeds were low (1-2 m/s) and wind direction was from the northern to north-northeast sector. In referring to the map in Figure 1, there is no apparent point sources of NO_x from that wind direction. Interstate Asphalt located to the north east, evident in Figure 1c as an open gravel pit, was not in operation during the study (*Mark Boyle, IDEQ, pers. communication*). Large point sources of NO_x from natural gas power plants are located to the west and north west. Interestingly the NO_x events of Sept 3 and Sept 9 had elevated levels of toluene and 2-butanone. The mixing ratios of NO_x decrease rapidly as the sun comes up suggesting the break up of a shallow mixed layer. The rapid decrease in monoterpenes mixing ratio with increasing solar radiation is also evident in Figure 4.2.1. There was no obvious impact of the CDA airport emissions at the Lancaster site. The airport is located to the south-southwest. Air traffic may have been too infrequent to notice a VOC plume.

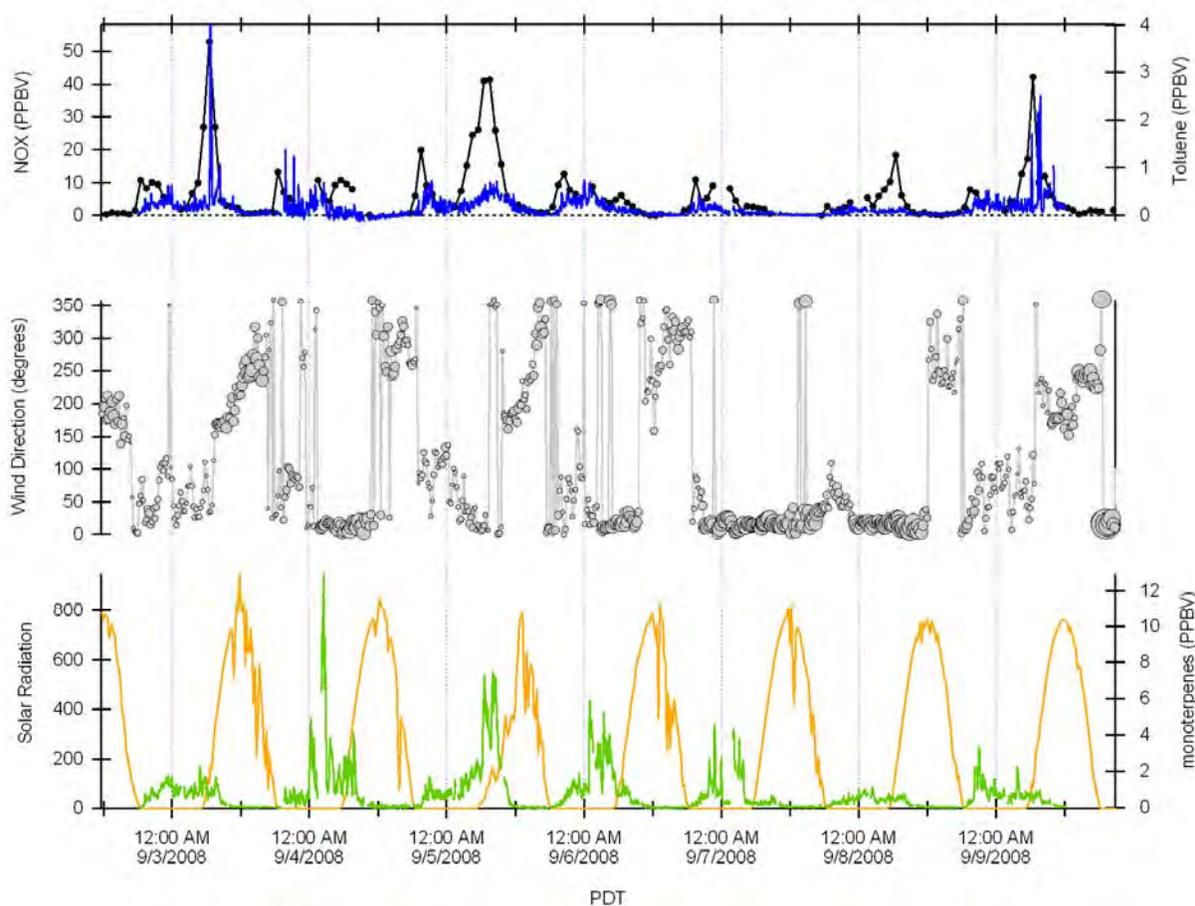


Figure 4.2.1 Lancaster NO_x events. Upper panel: NO_x (black circles) and toluene (blue trace). Middle panel: wind direction with symbols sized according to wind speed. Smallest symbols correspond to wind speed 1 m/s or smaller, largest symbols for wind speeds > 10 m/s. Lower panel: solar radiation (orange trace) and total monoterpene mixing ratio (green trace).

5. CONCLUSION

1. Hydrocarbon distribution at the Post Falls and Lancaster sites, as determined by canister analysis, is consistent with vehicle emissions being the dominant source of C₂-C₉ alkanes, alkenes, and aromatic species. Elevated concentrations of styrene, an industrial chemical, were observed on one occasion during the study at Post Falls. Biogenic hydrocarbons, in particular monoterpenes, were abundant at both sites.
2. Oxygenated species are the dominant volatile organic compounds in the Rathdrum Prairie region. Methanol is the most abundant VOC with mixing ratios ranging from 2 to 12 ppbv. Average methanol mixing ratio at Post Falls was 3.5 ppbv and at Lancaster 3.7 ppbv. Average acetaldehyde mixing ratios were 0.62 ppbv for Post Falls and 0.61 ppbv for Lancaster.
3. High total monoterpene mixing ratios were observed at night and early morning hours at Lancaster with mixing ratios up to 12 ppbv. Biogenic hydrocarbon chemistry is likely to be important for ozone and secondary organic aerosol generation production.
4. Three high NO_x events (NO_x > 30 ppbv) were observed at the Lancaster site during the early morning hours. These events could not be readily attributed to a particular source based on local wind direction. Wind speeds during these events were light (1-2 m/s) and generally from the northern sector.
5. VOC / NO_x ratios at Post Falls in the morning were typically less than 5 ppbC / ppbv. These are reasonably low ratios suggesting VOC limited chemistry. Low VOC / NO_x ratios were also observed at the Lancaster site for those morning samples with the highest NO_x mixing ratios. Both sites would appear to be VOC limited in term of ozone production.