

# Mount Wilson GHG Monitoring Gas Sampling and Analysis

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## Background

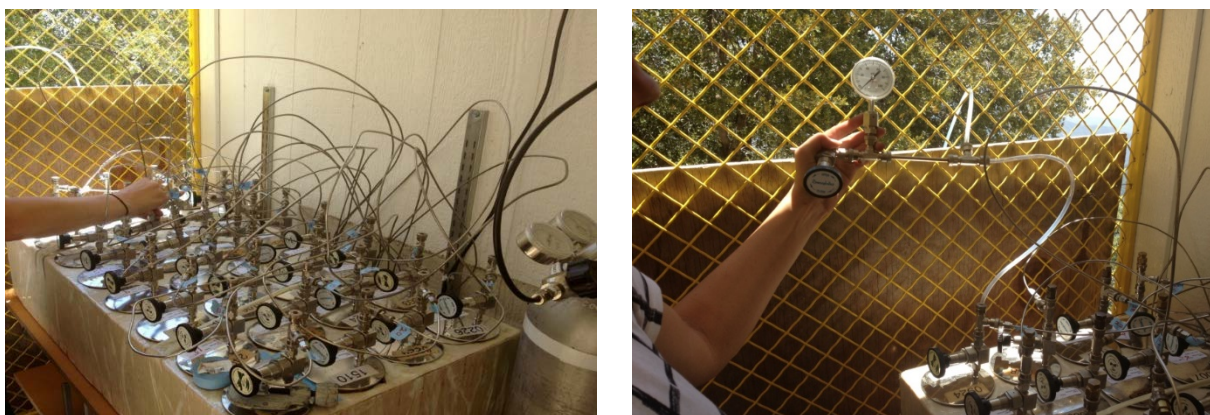
Mt. Wilson, which sits in the San Gabriel Mountains behind Sierra Madre, California (CA), peaks at 5,700 ft above sea level bounding the South Coast Air Basin (SoCAB) to the north. The SoCAB, which includes the Los Angeles megacity, is bounded by low mountain ranges on three sides, and the Pacific Ocean forms the fourth. The predominant wind patterns in the region are from off the coast heading northeast right to the base of Mt. Wilson. During the day time, the tropospheric boundary layer rises due to heating and air from the SoCAB reaches the mountains. As evening approaches, the temperature drops and the upslope cools, trapping the air in a much lower boundary layer.<sup>1</sup> This change in boundary layer height allows for sampling at Mt. Wilson during the daytime to be representative of the polluted troposphere in Los Angeles and at night be part of the upper free troposphere with only global background levels of air pollutants. For these reasons, several different studies have used Mt. Wilson as a sampling site to gather a full picture of the atmospheric chemistry of the SoCAB.<sup>2,3,4</sup> The goal of this sampling project was to monitor greenhouse gas (GHG) emissions from the SoCAB over a longer term (24 months) than previously achieved. This list of gases includes carbon dioxide, methane, chlorofluorocarbons (CFCs) and their replacements, hydrochlorofluorocarbons and hydrofluorocarbons (HCFCs and HFCs), as well as other constituents of air mass that typically derives from the SoCAB region.

## Sampling Methods

Each month, starting in June of 2014 and ending in May of 2016, 32 whole air samples were collected at the California Laboratory for Atmospheric Remote Sensing site at Mt. Wilson (34° 13' 15.28", -118° 3' 25.79"). Samples were collected in 1.9 L stainless steel canisters that are sealed with Swagelok Nupro metal bellows valves. Prior to each use, the canisters were flushed with high purity helium and then vacuumed down to ~.01 torr before being transported to the sampling site. Once at the Mt. Wilson site, each canister was connected to a stainless steel sampling line via a Swagelok "T-union". Each sampling line was connected to the Atmospheric Technology Model 8001 Automated Canister Sampler. This "auto-sampler" is capable of collecting integrated air samples at times specified by the user, without a technician being present. For this study, the sampling week started on the third Thursday of each month. Four samples were collected each day of that ensuing week at 11:00, 13:00, 15:00, and 17:00. These times were chosen to achieve

a broad picture of emissions that derived from the SoCAB during daytime hours when Mt. Wilson is within the boundary layer. The four remaining cans each month were used to sample at midnight to check for any local emissions and determine background air pollutant levels at that latitude. These samples were integrated over the course of one hour at an average flow rate of  $65 \text{ mL min}^{-1}$  which filled each canister to roughly 30 psi.

When setting up the canisters at the site, a dual bellows pump was used to pump and flush each of the 32 sampling lines. The lines were pressurized to 30 psi and then the valve was opened, allowing the pressurized sampling lines to return to ambient pressure as shown in Figure 1.



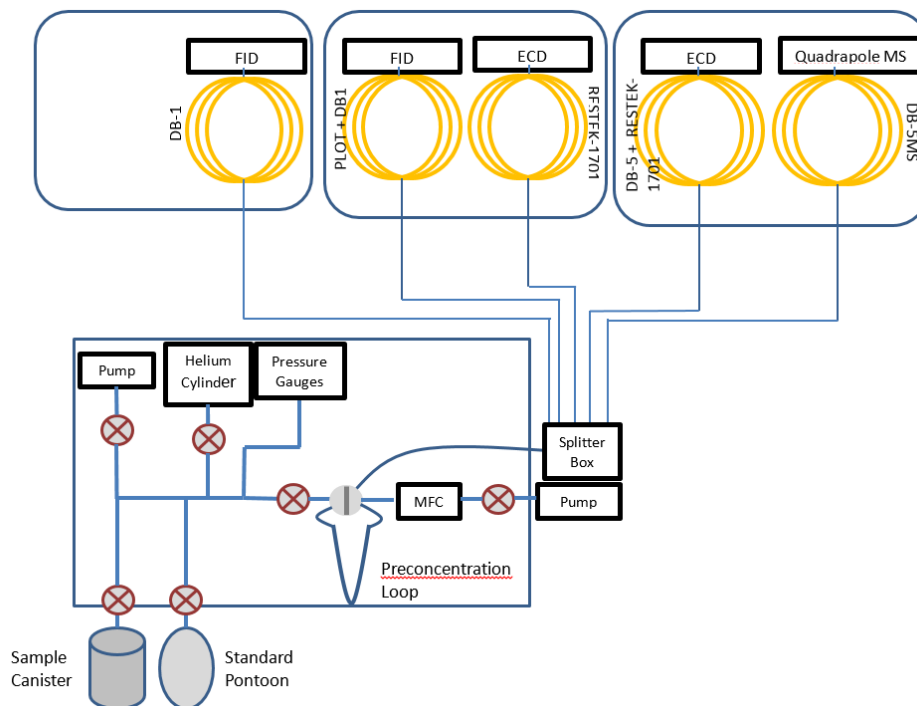
**Figure 1.** Images showing the canister sampling setup at Mt. Wilson. On the left, the 32 canisters are attached to the individual sampling lines prior to a plug being placed in each of the “T-unions”. The sampling lines are connected to the back of the auto-sampler, which is on the shelf below the canisters. The picture on the right shows the method by which the lines were flushed before each sampling month. The Teflon tubing leading outside of the caged area is connected to a bellows pump.

This was done three times to ensure that the lines were clean of any debris or stale air. Once the lines were flushed, they were reconnected to the “T-union” and a brass plug was added to the third opening. The canister valves were opened to allow them to be filled. This process, over 24 months of sampling, would theoretically yield a total of 768 different air samples. However, technical malfunctions and errors, reduced this number slightly. For the first, 14 months of sampling, a mechanical issues with two of the sampling lines, brought the total number of samples down to 30 each month. There were several instances when the O-ring in the “T-union” was damaged and not properly fixed prior to deployment. This resulted in a slow leak into the canister, which disqualified

the air samples from passing quality control checks. These leaks were detected by the auto-sampler when the noted pressure was above the threshold for an empty canister. Further, in April of 2016, an unexpected power outage occurred at the Mt. Wilson site during the sampling week. When power was restored, the auto-sampler had reset and lost the programming schedule. This resulted in only six samples being collected during that month. Due to these technical issues, 587 samples over two years were actually collected.

## Laboratory Analysis

Three separate gas chromatography (GC) systems were used for the quantitative detection of over 70 chemical compounds. The first system has been specifically designed with a flame ionization detector (FID) for methane (Accuracy:  $\pm 3$  ppb Precision:  $\pm 1\%$ ). The second system is capable of measuring carbon monoxide (Accuracy:  $\pm 7\%$  Precision:  $\pm 3\%$ ) and carbon dioxide (Accuracy:  $\pm 1$  ppm Precision:  $\pm 1\%$ ) via two GCs working in parallel. Finally, all other chemical compounds are detected via a trio of GCs working in parallel. There are 5 columns in this system, each of which is connected to a different detector as follows: a DB-1 column attached to an FID, PLOT+DB1 attached to an FID, RESTEK-1701 attached to an electron capture detector (ECD), DB5+RESTEK-1701 attached to an ECD, and DB-5 MS attached to a quadrupole mass spectrometer. The FIDs are used for hydrocarbon detection whereas the ECDs are used for the detection of halocarbons and alky nitrates. The mass spectrometer can be used for oxygenated species as well as a secondary (or sometimes tertiary) measurement for many hydro and halocarbons. The whole air samples are pre-concentrated with liquid nitrogen via a loop which is filled with glass beads to increase surface area upon which the compounds of interest can condense on. After passing 900 torr (2,170 mL at STP) of the whole air sample through the loop, the chemical compounds are re-volatilized by replacing the liquid nitrogen with near boiling water. The concentrated sample is then injected into the system and split to the five different columns. A diagram of this analytical system is shown in Figure 2.



**Figure 2.** The five column and three oven system used for the detection of over 70 different chemical compounds in whole air samples.

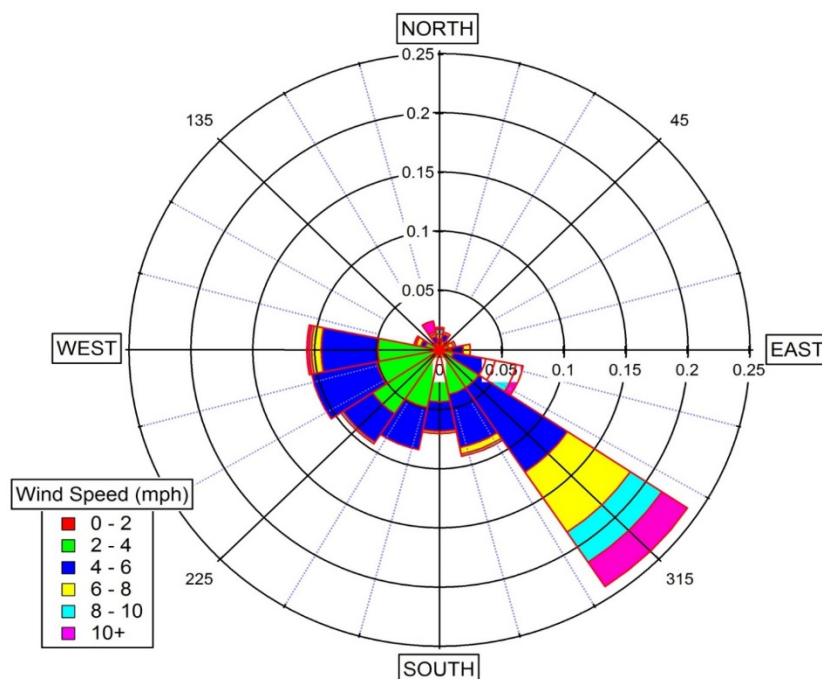
For hydrocarbons, precision ranges from 1-10% and accuracy is  $\pm 5\%$  (Table 1). For halocarbons, precision ranges from 1-3% and accuracy from 3-10%. Concentrations are determined via the peak areas and their relationship to a known standard containing all analytes that is run after every eight samples. The specifics of the entire system including oven heating sequences and standard preparation are found in Colman et al. **2001** and Simpson et al **2010**.<sup>5,6</sup> During the second month of sampling, four independent ambient samples were collected while the auto-sampler was collecting an integrated sample. This test was conducted to check for any chemical compounds that might be off gassed by the auto-sampler. The test concluded that the integrated and ambient air samples agreed well with each other with the exception of toluene. The integrated sample had an order of magnitude larger mixing ratio for toluene than did ambient canisters. For this reason, toluene mixing ratios are not reported. It was later discovered that the bellows pump used to flush the sampling lines off gasses toluene and will not be used in future studies.

**Table 1.** Statistical overview of the hydrocarbons and halocarbons used in analysis herein as measured by gas chromatography

<b>Compound</b>	Formula	LOD	Accuracy	% Precision
Carbon monoxide	CO	5 ppb	7%	3%
Carbon dioxide	CO <sub>2</sub>	1 ppb	1 ppm	1%
Methane	CH <sub>4</sub>	1 ppb	3 ppb	1%
Ethane	C <sub>2</sub> H <sub>6</sub>	3 ppt	5%	1%
Ethene	C <sub>2</sub> H <sub>4</sub>	3 ppt	5%	2%
Ethyne	C <sub>2</sub> H <sub>2</sub>	3 ppt	5%	1%
Propene	C <sub>3</sub> H <sub>6</sub>	3 ppt	5%	5%
Propane	C <sub>3</sub> H <sub>8</sub>	3 ppt	5%	3%
i-Butane	C <sub>4</sub> H <sub>10</sub>	3 ppt	5%	4%
n-butane	C <sub>4</sub> H <sub>10</sub>	3 ppt	5%	1%
i-pentane	C <sub>5</sub> H <sub>12</sub>	3 ppt	5%	1%
n-pentane	C <sub>5</sub> H <sub>12</sub>	3 ppt	5%	6%
Isoprene	C <sub>5</sub> H <sub>8</sub>	3 ppt	5%	3%
n-hexane	C <sub>6</sub> H <sub>14</sub>	3 ppt	5%	6%
2-methylpentane	C <sub>6</sub> H <sub>14</sub>	3 ppt	5%	2%
3-methylpentane	C <sub>6</sub> H <sub>14</sub>	3 ppt	5%	6%
n-heptane	C <sub>7</sub> H <sub>16</sub>	3 ppt	5%	9%
Benzene	C <sub>6</sub> H <sub>6</sub>	3 ppt	5%	7%
Ethylbenzene	C <sub>8</sub> H <sub>10</sub>	3 ppt	5%	5%
m/p-xylenes	C <sub>8</sub> H <sub>10</sub>	3 ppt	5%	4%
o-xylene	C <sub>8</sub> H <sub>10</sub>	3 ppt	5%	6%
1,2,4-trimethylbenzene	C <sub>9</sub> H <sub>12</sub>	3 ppt	5%	9%
<b>Halocarbons</b>				
CFC-12	CCl <sub>2</sub> F	10 ppt	3%	1%
CFC-11	CCl <sub>2</sub> F <sub>2</sub>	10 ppt	3%	1%
CFC-113	CCl <sub>2</sub> FCClF <sub>2</sub>	5 ppt	3%	1%
HFC-134a	CH <sub>2</sub> FCF <sub>3</sub>	1 ppt	10%	1%
HFC-152a	CHF <sub>2</sub> CH <sub>3</sub>	1 ppt	5%	3%
HCFC-22	CHF <sub>2</sub> Cl	2 ppt	5%	2%
HCFC-141b	CH <sub>3</sub> CCl <sub>2</sub> F	0.5 ppt	10%	2%
HCFC-142b	CH <sub>3</sub> CClF <sub>2</sub>	0.5 ppt	10%	2%
Chloroform	CHCl <sub>3</sub>	0.1	10%	3%
Methylchloroform	CH <sub>3</sub> CCl <sub>3</sub>	0.1	5%	1%
Dichloromethane	CH <sub>2</sub> Cl <sub>2</sub>	1	10%	1%
perchloroethylene	C <sub>2</sub> Cl <sub>4</sub>	0.01	10%	1%

## Summary

To understand the emission of greenhouse gases and other chemical compounds in the SoCAB, it is first important to ensure that samples collected are representative of the basin. Wind data was used to determine if a sample was influenced by the SoCAB. A wind rose plot showing the wind direction and speed at the beginning of the hour long sampling period for the samples collected here is shown in Figure 3.



**Figure 3.** Wind rose plot of winds arriving at the Mt. Wilson sampling site at the start of each daytime sample during the full two years of the study. The radial axis represents the fraction of the time the wind was blowing from a given direction, and the speed is color coded. Meteorological data was taken from the nearby Clear Creek weather station five miles east of Mt. Wilson.<sup>7</sup>

The prevailing winds are from the south and west which is where the SoCAB lies. During 86% of the daytime samples, the wind was blowing from across the SoCAB defined as from the W through the ESE.<sup>7</sup> This result shows that Mt. Wilson can be used to effectively sample downwind of the Los Angeles megacity. Samples coming from directions not associated with the SoCAB were removed before the following analysis was performed, however, the excluded samples may

provide insight into the air masses reaching the SoCAB during a Santa Ana wind event (not presented in this report).

## Hydrocarbon Results

A summary of the hydrocarbon mixing ratios seen in daytime samples that were influenced by the SoCAB is shown in Table 2. Daytime values range from global background to significant enhancements showing emissions stemming from the SoCAB. Also included in the table is the average daytime mixing ratio seen at Mt. Wilson in the 2007 pilot study. A quick comparison to the 2007 study shows that for compounds larger than ethane, average daytime concentrations have decreased nearly across the board. This quick look does not account for any changes in background levels over the eight years between studies, however, in many cases, the difference between 2007 and the present study is larger than the current background levels. Isopentane, for example, has seen a 350 pptv decrease since 2007 (54%). These results are encouraging and suggest that emissions reductions strategies put in place by the Air Resources Board are working for many hydrocarbons.

**Table 2.** Overview of the mixing ratios of selected hydrocarbons seen in the daytime samples collected at Mt. Wilson that were influenced by the South Coast Air Basin. Also included is the average daytime enhancement seen in the Mt. Wilson pilot study in 2007.

Species	Minimum (pptv)	Maximum (pptv)	Median (pptv)	Average (pptv)	Standard Deviation	IQR	2007 Average (pptv)
Methane (ppm)	1.798	2.362	1.925	1.932	0.057	0.060	1.883
Ethane	703	16471	2867	3110	1554	1547	2364
Ethene	59	8096	397	489	505	316	603
Ethyne	75	1993	491	542	293	328	811
Propane	216	9509	1197	1440	1006	931	1698
Propene	13	3432	87	132	213	67	106
i-butane	25	1774	204	247	190	182	349
n-butane	59	3701	396	501	417	376	609
i-Pentane	9	2052	236	297	229	255	647
n-Pentane	17	1251	146	179	140	128	252



Isoprene	13	8151	465	882	1135	840	782
2-methylpentane	Nd	583	63	78	65	65	110
3-methylpentane	Nd	370	50	59	45	48	95
n-hexane	Nd	418	55	67	51	52	89
benzene	37	396	122	134	60	76	186
ethylbenzene	4	167	29	37	28	31	62
m/p-xylene	7	248	50	62	44	48	124
o-xylene	3	116	21	27	20	22	52
1,2,4-trimethylbenzene	nd	59	9	11	7	7	18

## Halocarbon Results

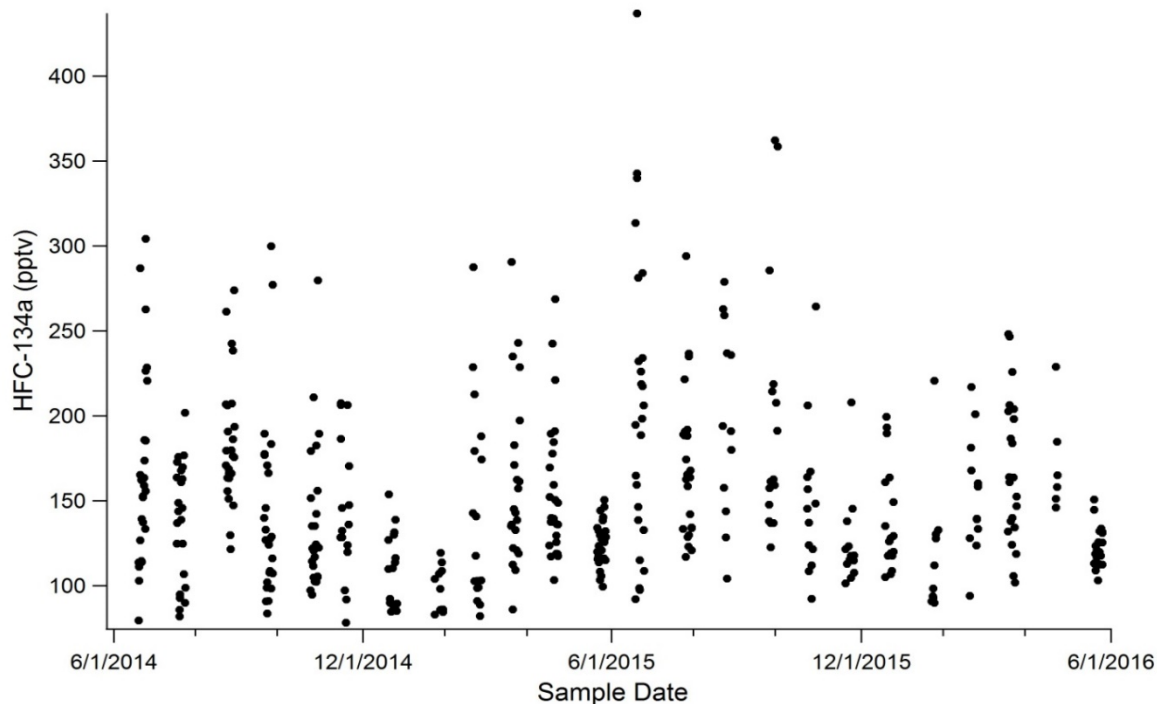
A summary of the daytime mixing ratios of select halocarbons in samples influenced by the SoCAB is shown in Table 4. As presented above, the average value from the 2007 study is included for reference. A quick look at the data suggests that many of the banned refrigerants are beginning to see their background levels decline. The CFC-11 daytime average mixing ratio is down 10% from 2007; this is very encouraging as the lifetime of CFC-11 is 45 years. HCFCs are also beginning to show decreased enhancements as bans and phase outs are put in place. This result should be used as a case study to support future phase out strategies as worthwhile.

**Table 4.** Overview of the mixing ratios of selected halocarbons seen in the daytime air samples collected at Mt. Wilson between May 2014 and June 2016. Also included is the average daytime enhancement seen in the Mt. Wilson pilot study in 2007.

Species	Minimum (pptv)	Maximum (pptv)	Median (pptv)	Average (pptv)	Standard Deviation	IQR	2007 Average (pptv)
CFC-12	513	564	530	531	11	15	559
CFC-11	225	276	238	238	7	9	263
CFC-113	72	83	74	75	2	2	81
H-1211	3.51	8.44	3.96	4.07	0.47	0.38	4.99
HFC-134a	78	437	139	153	53	60	106
HCFC-22	223	723	332	351	78	91	374

HCFC-142b	23	41	25	26	2	2	34
HCFC-141b	23	96	31	33	8	8	41
HFC-152a	12	454	112	126	74	92	106
CHCl3	9.40	41.17	21.53	21.80	5.11	6.03	17.8
CH3CCl3	2.70	7.01	3.84	3.99	0.72	0.92	15.6
CH2Cl2	36.7	439.9	102.5	112.9	51.4	53.9	97.9
C2Cl4	1.77	114.24	12.52	15.94	12.56	12.28	31.2
HFC-227ea	n.d.	3.69	1.80	1.81	0.56	0.58	n.a.
HFC-365mfc	n.d.	5.22	1.63	1.66	0.41	0.40	n.a.

Of the replacement refrigerants, HFC-134a and HFC-152a had higher daytime averages than in 2007. This is partly due to increasing background values (HFC-134a background mixing ratios increased over 20 pptv in this study alone) and the increased HFC use and leaks of within the SoCAB. Further, there is a distinct seasonality in the emission of 134a as seen in Figure 7. Mixing ratios peak in the summer months and decrease to a minimum in December.



**Figure 8.** Time series of HFC-134a mixing ratios at Mt. Wilson between June 2014 and May 2016. Emissions peak in the summer months and decrease in the winter and May. Over the two year study, background levels have also increased over 20 pptv.

In addition, it was observed that the lowest concentrations were observed in May each year, likely due to the differences in meteorology. This is an unexpected result and may be caused by the phenomenon known to Los Angeles area residents as June Gloom. Due to cool Pacific Ocean temperatures and a high pressure system passing over the region, a deep marine layer of stratus clouds can form off the coast of the region in May and June.<sup>17</sup> These clouds are pushed inland and cover most of the SoCAB. This boundary layer limits the amount of upslope venting and causes the samples taken during May of 2016 in particular to be cleaner than average. During such weather conditions, the need to turn on one's air conditioning unit also decreases, limiting chances for HFC-134a leaks from refrigeration units.

Finally, our ability to separate out new replacement HFCs was explored during this project. Starting in September of 2014, HFC-365mfc was successfully detected and quantitated by our quadrupole MS detector. Further, starting in September of 2015, HFC-227ea was quantitated. A summary of results of these two compounds is seen in Table 4. At this point, these gases are still

deemed exploratory and so the accuracy is  $\pm 50\%$ , however, our precision is much better and so trends in this data can still be noted. These gases have increasing background values suggesting their widespread use and that their emissions in urban areas should be monitored going forward.

## Conclusions

A two year monitoring study of emissions from the SoCAB was successfully completed between June 2014 and May of 2016. Integrated whole air samples were collected at Mt. Wilson each month to get a broad picture of VOC trends from the region. This study showed that sampling at Mt. Wilson is an effective way of gathering VOC data that represents part of SoCAB air that is relatively well-mixed. The data set is useful in resolving emission sources in the region as many tracer gases are quantitated and the long-term spread of the data allows for the observation of many different emissions events. New HFCs used in industry and refrigeration were quantitated for the first time on our system. This data allows for this study to be used as a baseline measure of their emission in an urban area as their use could potentially increase over time. The Mt. Wilson sampling site is an excellent proxy for having several monitoring stations around the region and should be used for future emissions studies.

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