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Multiyear trends in volatile organic compounds in Los Angeles, California: Five decades of decreasing emissions

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[1] Airborne measurements of volatile organic compounds (VOCs) were performed during CalNex 2010 (California Research at the Nexus of Air Quality and Climate Change) in the Los Angeles (LA) basin in May–June 2010 and during ITCT2k2 (Intercontinental Transport and Chemical Transformation) in May 2002. While CO₂ enhancements in the basin were similar between the two years, the $\Delta\text{CO}/\Delta\text{CO}_2$ ratio had decreased by about a factor of two. The $\Delta\text{VOC}/\Delta\text{CO}$ emission ratios stayed relatively constant between the two years. This indicates that, relative to CO₂, VOCs in the LA basin also decreased by about a factor of two since 2002. These data are compared with the results from various previous field campaigns dating back as early as 1960 and from the extensive air quality monitoring system in the LA basin going back to 1980. The results show that the mixing ratios of VOCs and CO have decreased by almost two orders of magnitude during the past five decades at an average annual rate of about 7.5%. Exceptions to this trend are the small alkanes ethane and propane, which have decreased slower due to the use and production of natural gas. A comparison with trends in London, UK shows that, due to stricter regulations at the time, VOC mixing ratios in LA decreased earlier than in London, albeit at a slower rate, such that typical mixing ratios in both cities in 2008 were at about the same level.

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1. Introduction

[2] Since the 1950s, the Los Angeles (LA) basin has been well known for its photochemically induced air pollution or urban smog with high ozone levels [Haagen-Smit, 1952; Renzetti, 1956]. The air quality problem in the LA basin or also called South Coast Air basin is so severe because of the very high population density (about 13 million people) and the very inefficient ventilation of the basin causing the pollution to be trapped inside. While the air quality in the LA basin has improved significantly, it is still designated as an ozone non-attainment area. Within this area, ozone (O₃) standards were exceeded on 102 days using national 8-h (0.075 ppm) and on 85 days using the state 1-h (0.090 ppm)

standard in 2010 (CARB, iADAM: Air Quality Data Statistics, 2012, <http://www.arb.ca.gov/adam/index.html>, 2012).

[3] California has always been one of the first states to implement air pollution controls ever since the introduction of the nation's first motor vehicle emission standards in 1966. These standards required pollution controls, such as air pumps that improve combustion efficiency. In 1970, the California Air Resources Board (CARB) required auto manufacturers to meet the first standards to control smog-forming hydrocarbon and nitrogen oxide (NO_x) emissions (CARB, History of Air Resource Board, 2011, <http://www.arb.ca.gov/knowzone/history.htm>; hereinafter CARB, online publication, 2011). CARB estimates that due to its regulations modern cars emit 99 percent less than vehicles did thirty years ago, but still over half of the state's VOC emissions come from gasoline and diesel-powered vehicles (CARB, online publication, 2011).

[4] Volatile organic compounds (VOCs) in the LA basin are mainly emitted by anthropogenic sources with vehicular traffic as the most important source. VOCs are oxidized in the atmosphere typically by reactions with the hydroxyl radical (OH) and produce a variety of secondary pollutants such as O₃, in the presence of sunlight and NO_x, and secondary organic aerosol (SOA). The O₃ forming potential of an air mass is strongly dependent on the VOC/NO_x ratio

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[Cardelino and Chameides, 1990; LaFranchi et al., 2011; Thornton et al., 2002] and to efficiently reduce O₃ in the LA basin, VOCs have been targeted for reduction.

[5] The earliest published measurements of non-methane hydrocarbons (NMHCs) in the LA basin date back to 1960 [Neligan, 1962]. Since then, there have been numerous other studies and an extensive monitoring network was started in the 1960s, which has been constantly improved and extended since then. Trends in pollutant concentrations and emissions have been investigated in LA and other U.S. cities in various studies [Ban-Weiss et al., 2008; Bishop and Stedman, 2008; Bishop et al., 2010; Dallmann and Harley, 2010; Harley et al., 2005; Parrish et al., 2011; Parrish et al., 2002], but they have mainly focused on NO_x, CO and particulate matter. Only few studies exist that investigate trends in total hydrocarbons or hydrocarbon ratios, most of which only look at vehicle exhaust [Bishop and Stedman, 2008; Fortin et al., 2005; Schmid et al., 2001; Stemmler et al., 2005; von Schneidemesser et al., 2010].

[6] In this paper we describe ambient VOC trends in the LA basin using three different data sources: (1) two NOAA aircraft campaigns in the LA basin: ITCT2k2 (Intercontinental Transport and Chemical Transformation) in 2002 and CalNex (Research at the Nexus of Air Quality and Climate Change) in 2010, (2) historical data sets from field intensives that are available from the literature and (3) data from the CARB monitoring network. The aircraft campaigns provide very detailed and accurate measurements for changes over the last decade, the literature data provide long-term trends back to 1960 and the monitoring network data trends for different locations within the LA basin back to 1990 for VOCs and back to 1980 for CO, O₃ and NO₂.

2. Experimental Setup

[7] During the months of May and June 2010, the NOAA WP-3D aircraft was based in Ontario, CA and conducted research flights in California as part of the CalNex field project. Flights were designed to investigate effects of urban and agricultural emissions on air quality and climate. Seven research flights were conducted in the LA basin during day- and nighttime. Gas phase measurements of VOCs such as benzene, toluene, formaldehyde and others that are used in our analysis, were made online by a proton-transfer-reaction mass spectrometer (PTR-MS) [de Gouw and Warneke, 2007; Warneke et al., 2011]. Airborne measurements of VOCs were made periodically throughout each flight using a whole air sampler (WAS) [Schauffler et al., 1999] and post-flight gas chromatographic analyses [Colman et al., 2001]. Carbon monoxide (CO) mixing ratios were measured by vacuum UV resonance fluorescence [Holloway et al., 2000]. Airborne CO₂ measurements were performed using wavelength-scanned cavity ring down spectroscopy (CRDS) manufactured by Picarro, Inc. The accuracy of the measurements for all the instruments used in the trend analysis was as follows: 20% for the PTR-MS, 10% for WAS and 5% for CO.

[8] In 2002, measurements using the WP-3 aircraft were performed in the LA basin as part of the ITCT2k2 study [Nowak et al., 2004]. The same relevant instrumentation as described above was used during this campaign except CO₂

was measured using a nondispersive infrared sensor (NDIR). Measurement accuracies were the same as in 2010.

[9] CARB has released 30 years of air quality data (1980–2009) with hourly, daily, and annual data. The Air Quality and Meteorological Information System (AQMIS) contains data measured from about 180 air quality sites and over 800 meteorological sites. VOC measurements are part of two monitoring networks: the non-methane hydrocarbons (NMHCs) and air toxics networks that are operated by CARB and the photochemical assessment monitoring stations (PAMS). Details on the measurement procedures, sampling intervals and data availability for VOCs, CO, ozone, NO₂ and organic carbon (OC) that are used in this analysis are publicly available through CARB (CARB, online publication, 2011). The CARB network NO₂ has a known sensitivity toward organic nitrates and HNO₃, but this does not influence any of the results presented here [Murphy et al., 2007; Winer et al., 1974]. CARB generally reports 1-h maximum ozone, 1-h maximum NO₂, 8-h maximum CO and annual averages for VOCs, because these values are used for regulatory purposes. We will most often use these maximum values for the trend analysis, but we will also use annual averages if necessary for comparisons.

3. VOC Decrease in the LA Basin

3.1. 2002 and 2010 Airborne VOC Data

[10] Results from the NOAA WP-3 flights on May 13, 2002 and May 4, 2010 are shown in Figure 1a to illustrate the significant reductions in VOC mixing ratios that took place in the last decade. Flight tracks are shown on top of the map of the LA basin and sections of each flight that were in the same geographical area, same time of day (around 14:00 LT) and inside the boundary layer are highlighted. A scatterplot of CO, as a tracer for pollution, versus CO₂, as a tracer for the amount of combustion, for all the data from the flight and the highlighted sections is shown in Figure 1b. Even though the CO₂ enhancements over background were comparable in the two years, about 25 ppm in 2002 and 35 ppm in 2010, the $\Delta\text{CO}/\Delta\text{CO}_2$ ratio for this flight track segment decreased from 24.5 ppbv/ppmv to 10.7 ppbv/ppmv. A reduction of about a factor of two of CO emissions compared to CO₂ over the last decade was also observed in various cities including LA (decrease between 56% and 71% dependent on the city) and is likely the result of continued improvements in function and durability of vehicle emission control systems [Bishop and Stedman, 2008].

[11] The scatterplots of some selected VOCs versus CO from the two highlighted flight segments are shown in Figure 2. Enhancement ratios of VOCs with CO for LA have been determined previously from the May 13, 2002 flight and compared to within a factor of two to measurements of other cities for all VOCs [Warneke et al., 2007]. The enhancement ratios of VOCs (slope versus CO from Figure 2) measured in both years and their changes from 2002 to 2010 are shown in Figure 3. Enhancement ratios from aromatics (e.g.: benzene and toluene), oxygenates (e.g.: acetaldehyde), alkenes and alkynes changed by less than 12% between the two years. Ethane and propane and other light hydrocarbon enhancement ratios increased by up to 50% since 2002. As can be seen in Figure 2, the small alkanes are not as well correlated with CO as all other VOCs. Acetone, a common oxidation

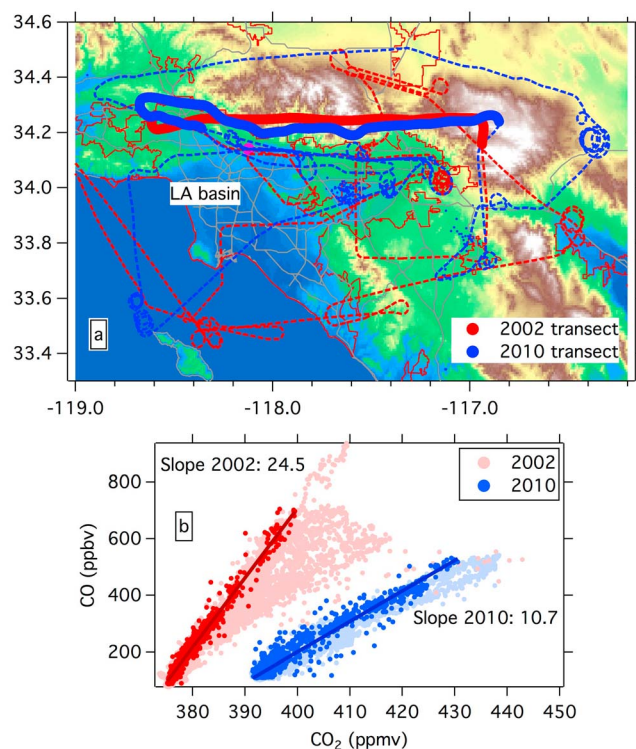


Figure 1. (a) Flight tracks of the NOAA WP-3 aircraft in the LA basin on May 13, 2002 during ITCT2k2 and on May 4, 2010 during CalNex 2010. Flight segments in similar meteorological conditions in the same geographical area are highlighted. (b) Scatterplot of CO versus CO₂ for both flights with linear fits of the data from the highlighted sections. The $\Delta\text{CO}/\Delta\text{CO}_2$ ratio decreased by about a factor of two from 2002 until 2010.

product of the alkanes, shows an increased enhancement ratio with CO (60% increase).

[12] The above analysis suggests that emissions of those VOCs that are predominantly emitted by vehicles have decreased together with CO by about a factor of two in eight years. The alkanes, which have additional large sources from natural gas use and production, decreased slower than CO. Acetone and possibly other ketones that are formed from alkanes also have not decreased as rapidly.

[13] Two different effects influence the uncertainty in the enhancement ratios of VOCs with CO and therefore the representativeness of the two flights as determined above. The first one is due to the accuracy of the measurements: 20% of the PTR-MS, 10% of the WAS and 5% of the CO measurements. The combined uncertainty due to the measurement accuracy is indicated in Figure 3a by the error bars on the 2002 data. Measurements and calibrations were done very similarly in 2002 and 2010, and therefore the change in enhancement ratios between the two years should not be influenced by the measurement accuracy. The second reason for the uncertainty in the enhancement ratios is the day-to-day variability, which is caused by processes such as temporal changes in emissions, meteorology, time of day, location and photochemical processing. In 2010 we performed 6 daytime and 4 night flights in the LA basin. Enhancement ratios determined for each flight varied by about 20%

for the light alkanes and by about 10% for all other compounds. Since we have only one flight in 2002, we do not know the day-to-day variability but assume that it was identical between the two years. The resulting uncertainty is indicated in Figure 3a by the error bars on the 2010 data. The day-to-day variability influences the comparison of the two years and the error bars in Figure 3b indicate the combined uncertainty for this effect.

3.2. VOC Measurements From Field Campaigns in the LA Basin Since 1960

[14] The LA basin has been the focus of many air quality campaigns since 1960 and LA is possibly the best-studied city in terms of VOC measurements in the United States and maybe even the world. The population and the number of vehicles have steadily increased and a proxy for the resulting CO₂ emission increase is the gasoline and diesel fuel sale in California since 1960 shown in Figure 4a. Fuel sales increased by about a factor of three over the last five decades. Despite the large increase in combustion related sources, the air quality improved significantly over the same time period as is demonstrated in Figures 4b–4i. In Figure 4b the

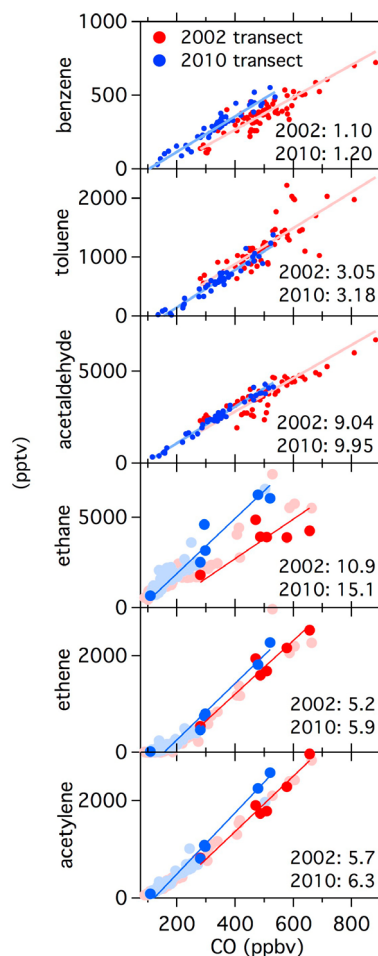


Figure 2. Scatterplots of VOC versus CO for the flights shown in Figure 1 with the highlighted sections in darker colors. Benzene, toluene and acetaldehyde data are from the PTR-MS. Ethane, ethene and ethyne data are from the WAS.

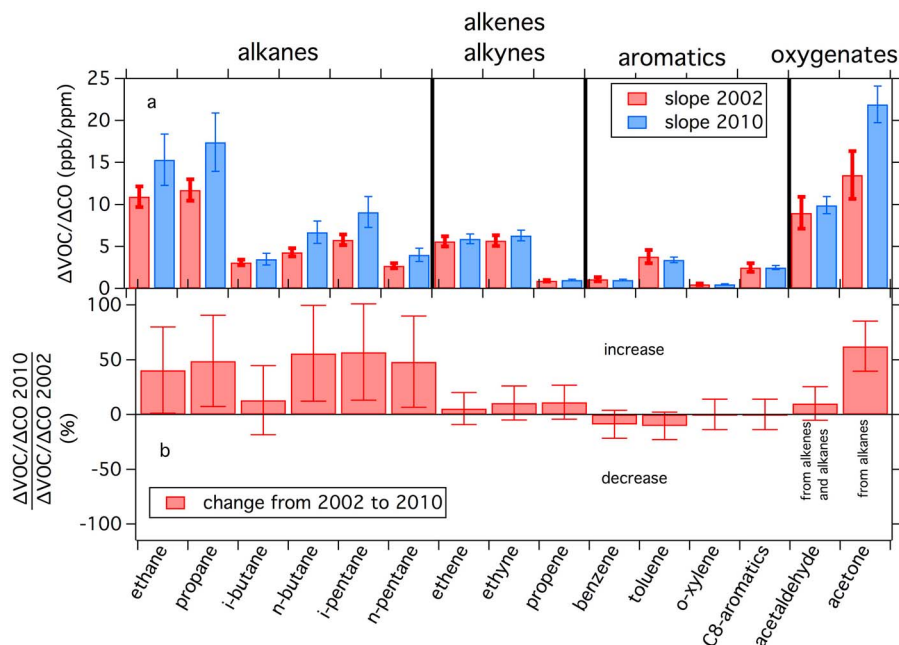


Figure 3. (a) Enhancement ratios of VOCs with CO ($\Delta\text{VOC}/\Delta\text{CO}$) from 2002 to 2010. The error bars on the 2002 data represent the measurement accuracies, the error bars on the 2010 data the day-to-day variability. We assume the same day-to-day variability in 2002 as in 2010. (b) Change in enhancement ratios from 2002 to 2010. Alkenes/CO and aromatics/CO ratios changed by less than 12% and alkane/CO and acetone/CO ratios increased by up to 60% between 2002 and 2010. The error bars indicate the combined uncertainties.

1-h maximum ozone values in the LA basin from the CARB monitoring network shows a significant decrease from a maximum value of 710 ppbv in 1966 to 143 ppbv in 2010. From 1965 until 1998 the decrease was about 11 ppbv/year and slower afterwards with less than 2 ppbv/year.

[15] In Figures 4c–4i literature data are added from multiple field campaigns conducted by many different groups close to LA downtown. The location, campaign name, and literature reference of the campaigns used in Figure 4 are given in Table 1. Figure 4 is not meant to be a complete list of all field campaigns conducted in the LA basin, but they were selected for easy data availability, location and time, so that there are data spread out over five decades containing many species relevant to this study. From those literature data typical daytime mixing ratios of CO and various VOCs are estimated. Influences on the mixing ratios such as the time of year or possible pollution episodes during the campaigns are not explicitly accounted for. This means that the uncertainty for each data point is large, but this uncertainty is still small compared to the large trends that are seen in the data. Typical daytime mixing ratios of CO, shown in Figure 4c, decreased by almost two orders of magnitude from close to 20 ppm in the 1960s to about 400 ppbv in 2010. Figures 4d–4f show various VOCs on a linear scale and to better demonstrate the decrease over the last decade on a logarithmic scale in Figures 4g–4i. All VOCs show the same decreasing trend as CO, especially after the introduction of the catalyst in 1976 mixing ratios decrease strongly at first and then slower but steadily since then. The trends of the VOCs and CO from Figure 4 are investigated in Figure 5 by determining the slope of the natural log of the data. The slope of this fit represents

the percent change per year. In Figure 5 a decreasing trend of 7.5% is indicated with the solid red line and all compounds display a trend in the same range. Values for all compounds are given in Table 2.

3.3. VOC Measurements From the CARB Monitoring Network

[16] Figure 6a shows the locations of all the monitoring sites in and around the LA basin, which is the South Coast Air Basin air quality-monitoring area. Four sites are highlighted from which data will be discussed in more detail. Figure 6b shows the daily and the annual average CO from 1980 until 2008 at the LA North Main site. Strong seasonal changes are observed for CO, but the decreasing trend is very clear for those three decades. The 8-h maximum CO and the 1-h maximum O_3 and NO_2 and a basin wide average of all sites are shown in Figures 6c–6e. There is a large variability for the three compounds between all the sites, which is expected due to the different locations of the sites with some, like LA North Main, located in downtown LA and others located outside the basin and even upwind on Catalina Island. The individual sites and the LA basin wide averages exhibit a very clear trend with 8-h maximum CO mixing ratios dropping by about an order of magnitude and O_3 and NO_2 by about a factor of two during those three decades. Fires had a significant influence on the LA basin. One example is the 2007 Southern California wildfire and high winds extreme event that burned over a half-million acres. Fire influences are not removed from the monitoring network data and are likely the reason for some of the observed variability, but are unlikely to influence the trends.

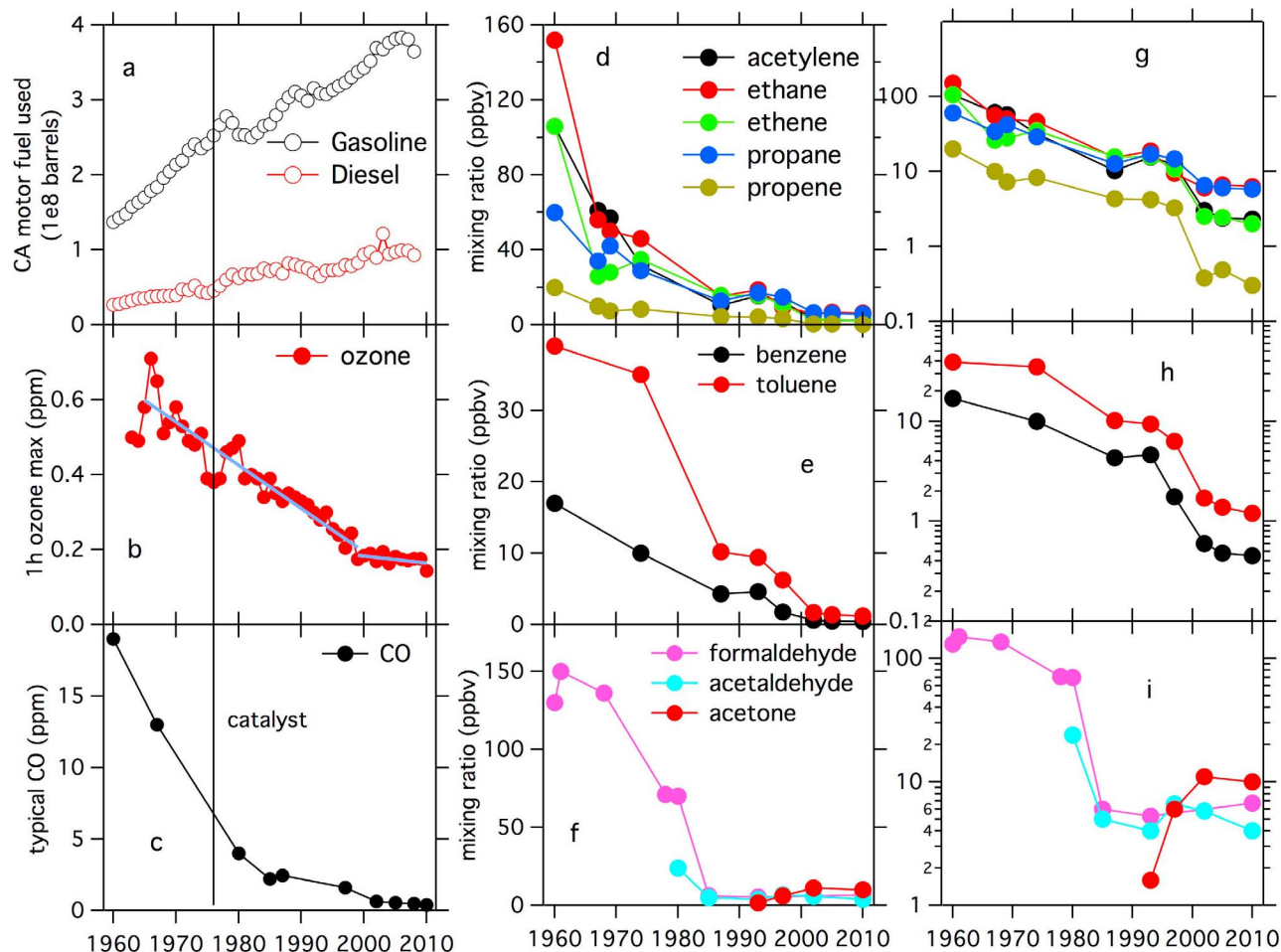


Figure 4. Trends since 1960: (a) California fuel (gasoline and Diesel) sales; (b) 1-h ozone maximum mixing ratios in the LA basin. (c–f) Typical mixing ratios estimated from published data from various campaigns close to downtown LA. References are given in Table 1. (g–i) Same as Figures 4d–4f on a logarithmic scale.

[17] Figure 7 shows annual averages of VOC data until 2008 from the toxics network from three sites. On two of those sites other NMHC were also measured. The locations of those stations are indicated in Figure 6a. Those sites were chosen as examples because of their location and data availability. The toxics network was established earlier and therefore the data coverage is better compared to the NMHCs. VOC emissions are spread out over the whole LA basin, but the main emissions sources are closer to LA downtown, so that LA North Main and Burbank are mostly dominated by fresh emissions and Azusa and especially Riverside are relatively more influenced by aged emissions that are transported during the day from the upwind areas further west. The difference in photochemical processing for those sites can be seen for example in the higher mixing ratios of primary CO closer to downtown and higher ozone mixing ratios further east in the LA basin. The CARB network data show similar decreasing trends for all VOCs as the LA basin field campaigns discussed earlier.

[18] The Burbank site, has the most complete data coverage of compounds important for this analysis, is located close to the main emissions region and shows persistently

some of the highest primary pollutant mixing ratios in the LA basin. Therefore we have used Burbank as an example of all the CARB monitoring sites for a detailed analysis of the trends. The percent change per year in Burbank for many VOCs and CO were determined in the same way as in

Table 1. Data Source for Results in Figures 4 and 5 and Table 2^a

Year	Literature	Location
1960	[Neligan, 1962]	Downtown LA
1961	[Grosjean, 1982]	Downtown LA
1967	[Gordon et al., 1968]	Downtown LA
1968	[Grosjean, 1982]	Downtown LA
1969	[Mayrsohn et al., 1975]	Downtown LA
1974	CARB data collection	Downtown LA
1978	[Grosjean, 1982]	Downtown LA
1980	[Grosjean, 1982]	Claremont
1985	[Grosjean, 1988]	Claremont
1987	[Lawson, 1990]	Downtown LA
1993	[Fraser et al., 1997]	Downtown LA
1997	CARB data collection SCOS97	Anaheim
2002	[Warneke et al., 2007]	ITCT2k2, aircraft
2005	[Baker et al., 2008]	Downtown LA
2010	CalNex 2010	aircraft

^aGiven are year campaigns took place, references and campaign location.

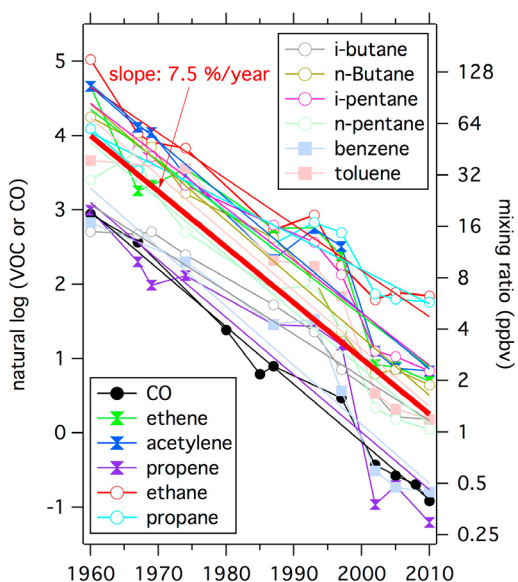


Figure 5. Natural logarithm of the data in Figures 4c–4f together with linear fits on the left axis and mixing ratios on the right axis. The solid red line indicates a 7.5%/year decrease.

Figure 5. Table 2 gives the percent change per year and the annual average mixing ratios for 2008. The range of data availability is also shown in Table 2. CO is continuously available since 1980, aromatics measured with the toxics

network since 1990 and hydrocarbons measured with the NMHC network since 2001. The LA basin field campaigns displayed a trend of close to 7.5%/year for all investigated compounds since 1960. The trends in Burbank for the shorter time periods and a more comprehensive set of compounds are more variable, where alkenes decrease in roughly the same rate as CO with 6.3%/year, small alkanes generally decrease slower, and aromatics faster. Parrish *et al.* [2002] observed trends in CO from 1989 to 1999 ranging from 4.8 to 6.3%/year for various U.S. cities and Burbank is within that range. As concentrations in the atmosphere decrease, for some species the atmospheric backgrounds, defined as the concentration in clean marine air coming into the basin, become a significant part of the ambient concentration. This reduces the decrease in %/year, so the absolute decrease in long-lived species that have higher atmospheric backgrounds could be smaller than for more reactive VOCs.

4. Constant VOC Emission Ratios

[19] As shown for example by Bishop and Stedman [2008], vehicle emissions of hydrocarbons have strongly and steadily decreased with vehicle model year from 1986 until the end of their measurements in 2003. Continuing fleet improvements and fleet turnover will continue to decrease the emissions of VOCs even further. Combustion in gasoline and diesel engines is the most important source of air pollution in the LA basin. According to CARB emission inventory data, in the LA basin in 2008 mobile source emissions were responsible for 89% of total NO_x , 52% of

Table 2. Annual Average VOC Mixing Ratios in 2008 and VOC Trends in the LA Basin and in London, UK^a

Compound	Change: LA Basin Campaigns (%/year)	Data Coverage Burbank CARB Network	2008 Annual Average Burbank CARB Network (ppbv)	Change: Burbank CARB Network (%/year)	2008 Annual Average London (ppbv)	Change: London 1998–2008 (%/year)
CO	–7.8	1980–2008	540	–6.38 ^b	530	–12
ethane	–6.2	2001–2008	10.3	–1.3	7.1	–4
propane	–4.6	2001–2008	7.05	–1.8	2.7	–3
i-butane	–5.8	2001–2008	1.59	–2.8	1.2	–14
n-butane	–7.8	2001–2008	2.86	–6.2	2	–17
i-pentane	–7.1	2001–2008	3.46	–7.3	1.6	
n-pentane	–7.6	2001–2008	1.3	–6.6	0.54	–12
n-hexane		2001–2008	0.59	–3.2	0.15	–14
n-heptane		2001–2008	0.36	–1	0.087	–16
n-octane		2001–2008	0.26	–2.7	0.036	
i-hexane		2001–2008	0.91	–10.9		
acetylene	–7.7	2001–2008	2.81	–8.9	1.3	–15
ethene	–6.9	2001–2008	3.86	–8.4	2.4	–20
propene	–7.7	2001–2008	0.98	–6.5	0.72	–20
1-butene		2001–2008	0.12	–15	0.17	–17
1-pentene		2001–2008	0.1	–6.5		
1-hexene		2001–2008	0.06	–8.3		
trans-2-butene		2001–2008	0.06	–12.6		
cis-2-butene		2001–2008	0.07	–10.3		
benzene	–7.9	1990–2008	0.57	–11.6	0.32	–26
toluene	–7.8	1990–2008	2.01	–8.7	1	–22
mp-xylene		1993–2008	1.03	–8.5	0.79	–20
o-xylene		1990–2008	0.36	–9	0.2	–25
ethylbenzene		1990–2008	0.26	–8	0.14	–23
123-trimethylbenzene		2001–2008	0.05	–15.9		
124-trimethylbenzene		2001–2008	0.12	–21.9		
135-trimethylbenzene		2001–2008	0.14	–8.4		

^aThe data sources for the LA basin campaigns are given in Table 1 and data are shown in Figure 4. London data are taken from von Schneidmesser *et al.* [2010].

^bCO change 1998–2008: 11.9%/year, 1980–1998: 4.0%/year.

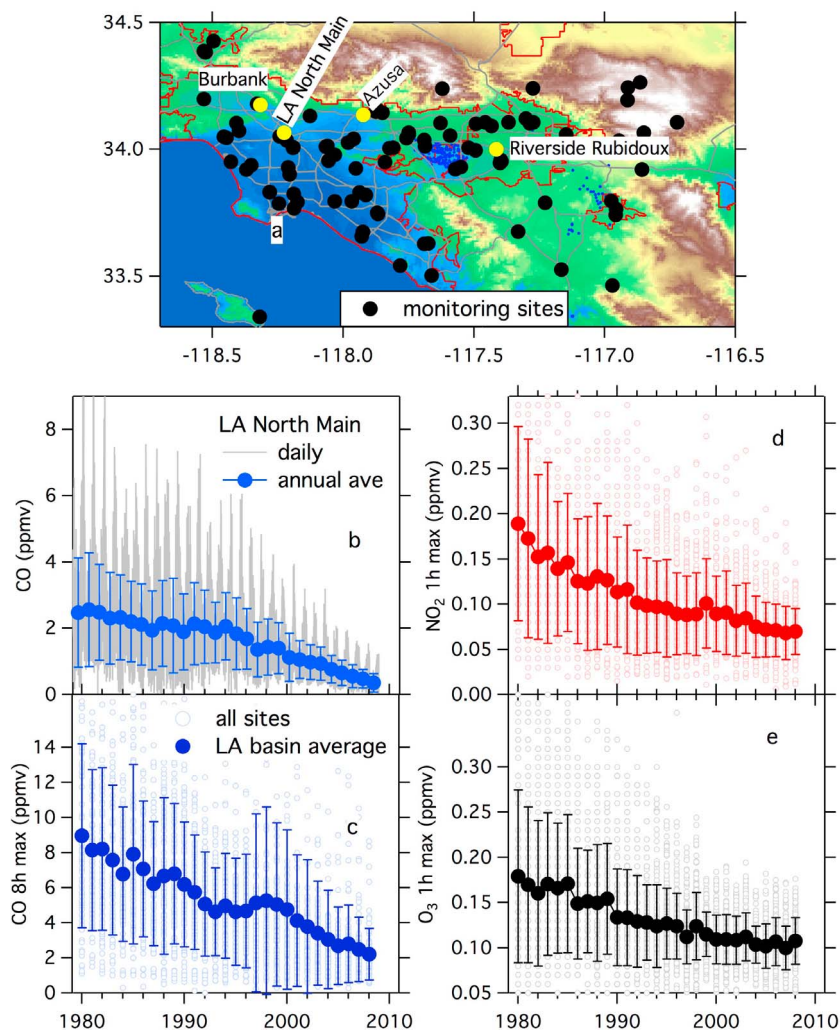


Figure 6. (a) Map of the monitoring sites in the LA basin. Data from the highlighted sites (in yellow) are used for detailed analysis. (b) Daily and annual average CO at LA North Main. (c) CO 8-h maximum from all sites in Figure 6a and their average from 1980 until 2008. (d) NO₂ 1-h maximum. (e) O₃ 1-h maximum. Error bars represent the 1-sigma standard deviation.

reactive organic gases (ROG), 90% of CO, and 30% of PM_{2.5} (CARB, California Air Basin Map, 2009, <http://www.arb.ca.gov/ei/maps/statemap/abmap.htm>). In the LA basin VOCs and CO decreased together at roughly the same rate. Figure 8 shows the VOC/CO ratio, where CO is available, or the VOC/acetylene ratio for all the data from the field campaigns shown in Figure 4. In this ratio the atmospheric background of CO has not been taken into account, which will influence the ratio as the mixing ratios approach background levels. Acetylene has often been used as a marker for urban emissions in place of CO, where no CO data were available [Warneke *et al.*, 2007]. Despite the decrease of close to two orders of magnitude, the ratios and therefore the VOC mix are relatively constant for all VOCs since 1960 in the LA basin. Even after the introduction of the three-way catalyst in the 1970s and various fuel composition changes in the 1990s [Kirchstetter *et al.*, 1996, 1999a] the ratios stayed relatively constant. The detailed look at the Burbank data in Table 2 shows that there were certainly variations in the VOC/CO ratios on shorter time

scales for some compounds, but on average the ratios have stayed remarkably constant since 1960. Only the ethane and propane ratios have increased in the past decade as was discussed earlier. The VOC/CO ratios from the toxics network and VOC/acetylene ratios from the NMHC network (not shown here) demonstrate the same constant trend for all VOCs. Alkane ratios seem to increase as well, but time series are rather short for a more detailed analysis.

[20] The main source for CO in the LA basin is light duty-gasoline vehicles [Harley *et al.*, 2005] and, as can be seen from the dramatic decrease in CO and VOC mixing ratios, a lot of progress has been made in emissions reduction. As the gasoline vehicle emissions continue to decrease, other sources of VOCs can gain relative importance, which is the case for the alkanes. The ratios of the small alkanes ethane and propane (Figures 3, 4 and 7) with CO show a clear increase since the mid 1990s, indicating a much smaller reduction in emissions for those compounds. Small alkanes have large area sources from the use and the production of natural gas. Before the 1990s the vehicle emissions even for

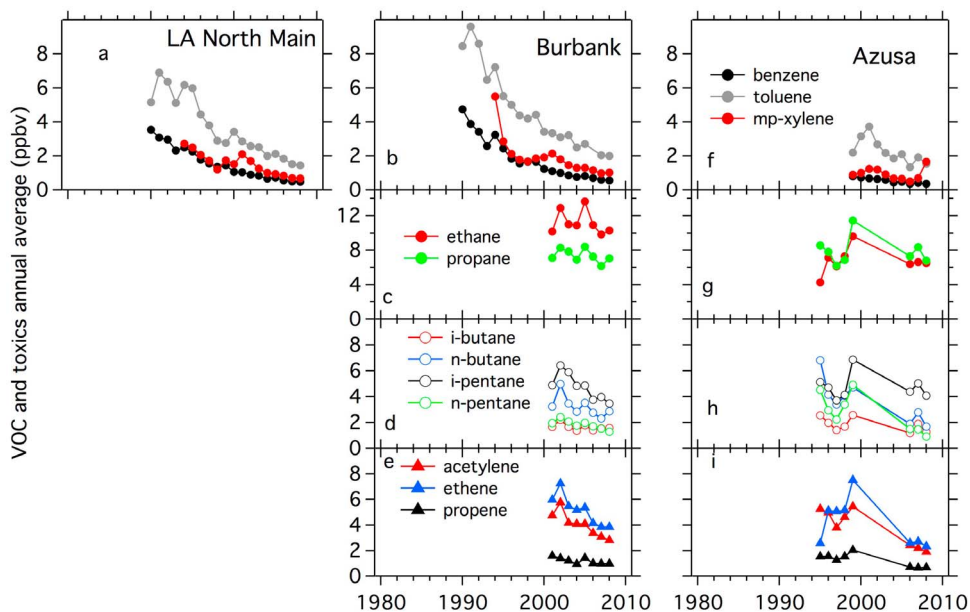


Figure 7. Annual averages of various VOCs from LA North Main, Burbank and Azusa.

the alkanes were so dominant that the ratios with CO were not significantly influenced by other sources. Another indication that alkanes have other major sources besides vehicles is the lower correlation coefficients with CO from the aircraft measurements in 2002 and 2010 as shown in Figure 2. One of the main atmospheric degradation products of the alkanes are ketones such as acetone [Sommariva *et al.*, 2011]. The acetone/CO ratios show similar trends as the alkanes. Aldehydes like acetaldehyde are more efficiently produced from alkenes than alkanes [Sommariva *et al.*, 2011] and possible as a result show the same trends as CO. Another potential increase of acetaldehyde comes from the oxidation of ethanol in fuel used in the U.S., but no increase since 2002 was detected [de Gouw *et al.*, 2012].

5. Comparison With Trends in Other Cities

[21] The trends in ambient urban mixing ratios of CO and VOCs from the LA basin are compared to recently published trends from London, UK in Figure 9 and Table 2 [von Schneidmesser *et al.*, 2010]. The data in London were collected at a curbside downtown location in the Marylebone Road between 1998 and 2008 and are therefore best compared to the LA North Main or Burbank sites. Annual average CO and VOC mixing ratios in London are given in Table 2 together with the percent change from 1998 to 2008. VOCs and CO are calculated back to 1998 and selected species are shown in Figure 9. Annual average CO mixing ratios and trends are surprisingly similar in London and LA downtown from 1998 to 2008: 540 ppbv and 11.9%/year in Burbank and 530 ppbv and 12%/year in London, respectively. From 1980 to 1998 the CO decrease in Burbank was smaller with about 4%/year. VOC mixing ratios in 2008 were also quite similar with LA generally a little bit higher, but trends were quite different. In London mixing ratios in 1998 were clearly higher, but the decrease since 1998 was faster.

[22] California started early and aggressively to implement regulations reducing emissions of VOCs from vehicles. For example, in 1994 oxygenated fuels were introduced that

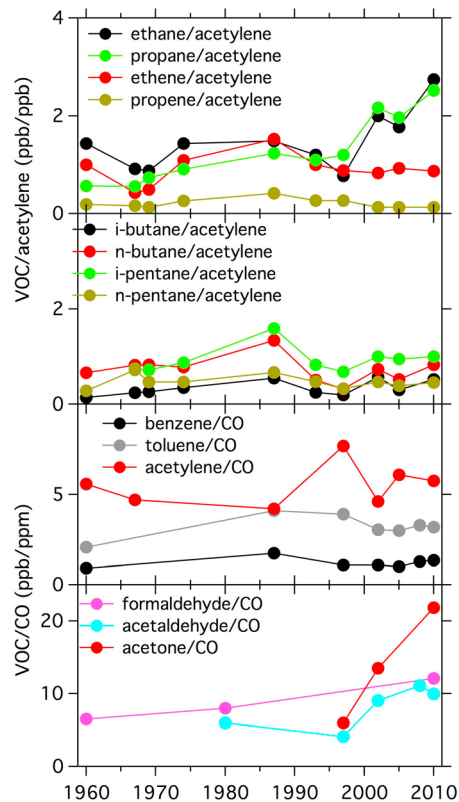


Figure 8. VOC/acetylene and VOC/CO ratios from the data shown in Figures 4c–4f from 1960 until 2010. All ratios are relatively constant except ethane and propane from natural gas use and production together with their oxidation product acetone increase.

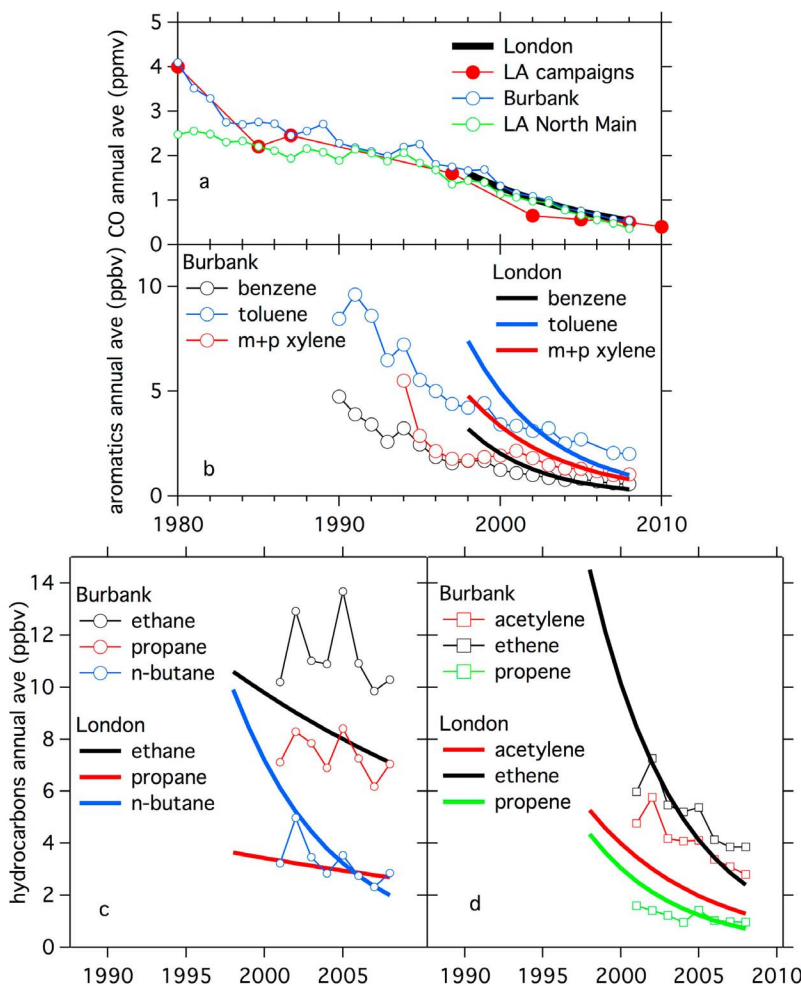


Figure 9. Comparison of LA with London, UK: (a) Annual average CO in the LA basin from 1980 until 2010 and in London from 1998 until 2008. (b) Annual averages of aromatics in Burbank from 1990 until 2008 and in London. (c) Annual averages of alkanes in Burbank from 2001 until 2008 and in London. (d) Annual averages of ethene, propene and acetylene in Burbank and in London. London data are from von Schneidemesser *et al.* [2010].

helped decrease VOC emissions [Kirchstetter *et al.*, 1996] and in 1996 reformulated gasoline further reduced emissions [Kirchstetter *et al.*, 1999a, 1999b]. It seems from Figure 9 that these measures have helped reduce VOCs earlier, so that mixing ratios prior to 2005 were lower in the LA basin than in London, even though pollution gets trapped in the LA basin for multiple days and can build up to much higher levels than without trapping.

6. Conclusions

[23] Detailed VOC measurements from two aircraft campaigns in the LA basin in 2002 and 2010 were used to show that VOC emissions have been reduced by about a factor of two in those eight years. Literature data and data from the monitoring network in the LA basin were used to show that the mixing ratios of VOCs and CO have declined almost two orders of magnitude since 1960 at an average annual rate of about 7.5% even though the fuel sale in California increased by about a factor of three over the same time period. VOC/

CO ratios have been remarkable constant in this time period despite the introduction of the catalyst and reformulated and oxygenated gasoline. This indicates that the main VOC source in the LA basin is likely gasoline vehicle emission. Ethane and propane have decreased more slowly than all other VOCs indicating that after the large reduction in vehicle emissions other sources such as the use and production of natural gas can have a significant contribution to ambient mixing ratios.

[24] A comparison with London found that VOC mixing ratios in 2008 are at about the same level in both cities, but in London a much stronger decrease from higher mixing ratios in 1998 has led to the current mixing ratios. This suggests that the early implementation of VOC emission reduction strategies in California clearly has led to improved air quality earlier on compared to London.

[25] Looking at the strong decreasing trends even in the past few years, a further reduction of VOCs is likely and certainly will help to decrease total ozone and SOA production in and downwind of the LA basin in the future.

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References

- Baker, A., A. J. Beyersdorf, L. Doezema, A. Katzenstein, S. Meinardi, I. J. Simpson, D. R. Blake, and F. S. Rowland (2008), Measurements of nonmethane hydrocarbons in 28 United States cities, *Atmos. Environ.*, *42*, 170–182, doi:10.1016/j.atmosenv.2007.09.007.
- Ban-Weiss, G., J. McLaughlin, R. Harley, M. Lunden, T. W. Kirchstetter, A. Kean, A. Strawa, E. Stevenson, and G. Kendall (2008), Long-term changes in emissions of nitrogen oxides and particulate matter from on-road gasoline and diesel vehicles, *Atmos. Environ.*, *42*(2), 220–232, doi:10.1016/j.atmosenv.2007.09.049.
- Bishop, G. A., and D. H. Stedman (2008), A decade of on-road emissions measurements, *Environ. Sci. Technol.*, *42*(5), 1651–1656, doi:10.1021/es702413b.
- Bishop, G. A., A. M. Peddle, D. H. Stedman, and T. Zhan (2010), On-road emission measurements of reactive nitrogen compounds from three California cities, *Environ. Sci. Technol.*, *44*(9), 3616–3620, doi:10.1021/es903722p.
- Cardelino, C. A., and W. L. Chameides (1990), Natural hydrocarbons, urbanization, and urban ozone, *J. Geophys. Res.*, *95*(D9), 13,971–13,979, doi:10.1029/JD095iD09p13971.
- Colman, J. J., A. L. Swanson, S. Meinardi, B. C. Sive, D. R. Blake, and F. S. Rowland (2001), Description of the analysis of a wide range of volatile organic compounds in whole air samples collected during PEM-Tropics A and B, *Anal. Chem.*, *73*(15), 3723–3731, doi:10.1021/ac010027g.
- Dallmann, T. R., and R. A. Harley (2010), Evaluation of mobile source emission trends in the United States, *J. Geophys. Res.*, *115*, D14305, doi:10.1029/2010JD013862.
- de Gouw, J. A., and C. Warneke (2007), Measurements of volatile organic compounds in the Earth's atmosphere using proton-transfer-reaction mass spectrometry, *Mass Spectrom. Rev.*, *26*(2), 223–257, doi:10.1002/mas.20119.
- de Gouw, J. A., et al. (2012), Increasing atmospheric burden of ethanol in the United States, *Geophys. Res. Lett.*, *39*, L15803, doi:10.1029/2012GL052109.
- Fortin, T. J., B. J. Howard, D. D. Parrish, P. D. Goldan, W. C. Kuster, E. L. Atlas, and R. A. Harley (2005), Temporal changes in US benzene emissions inferred from atmospheric measurements, *Environ. Sci. Technol.*, *39*(6), 1403–1408, doi:10.1021/es049316n.
- Fraser, M. P., G. R. Cass, B. R. T. Simoneit, and R. A. Rasmussen (1997), Air quality model evaluation data for organics. 4. C₂–C₃₆ non-aromatic hydrocarbons, *Environ. Sci. Technol.*, *31*(8), 2356–2367, doi:10.1021/es960980g.
- Gordon, R. J., H. Mayrsohn, and R. M. Ingels (1968), C₂–C₅ hydrocarbons in the Los Angeles atmosphere, *Environ. Sci. Technol.*, *2*(12), 1117–1120, doi:10.1021/es60023a002.
- Grosjean, D. (1982), Formaldehyde and other carbonyls in Los Angeles ambient air, *Environ. Sci. Technol.*, *16*(5), 254–262, doi:10.1021/es00099a005.
- Grosjean, D. (1988), Aldehydes, carboxylic-acids and inorganic nitrate during NSMCS, *Atmos. Environ.*, *22*(8), 1637–1648, doi:10.1016/0004-6981(88)90391-5.
- Haagen-Smit, A. J. (1952), Chemistry and physiology of Los Angeles smog, *Ind. Eng. Chem.*, *44*, 1342–1346, doi:10.1021/ie50510a045.
- Harley, R. A., L. C. Marr, J. K. Lehner, and S. N. Giddings (2005), Changes in motor vehicle emissions on diurnal to decadal time scales and effects on atmospheric composition, *Environ. Sci. Technol.*, *39*(14), 5356–5362, doi:10.1021/es048172+.
- Holloway, J. S., R. O. Jakoubek, D. D. Parrish, C. Gerbig, A. Volz-Thomas, S. Schmitgen, A. Fried, B. Wert, B. Henry, and J. R. Drummond (2000), Airborne intercomparison of vacuum ultraviolet fluorescence and tunable diode laser absorption measurements of tropospheric carbon monoxide, *J. Geophys. Res.*, *105*(D19), 24,251–24,261, doi:10.1029/2000JD900237.
- Kirchstetter, T. W., B. C. Singer, R. A. Harley, G. B. Kendall, and W. Chan (1996), Impact of oxygenated gasoline use on California light-duty vehicle emissions, *Environ. Sci. Technol.*, *30*(2), 661–670, doi:10.1021/es950406p.
- Kirchstetter, T. W., B. C. Singer, R. A. Harley, G. R. Kendall, and J. M. Hesson (1999a), Impact of California reformulated gasoline on motor vehicle emissions. 2. Volatile organic compound speciation and reactivity, *Environ. Sci. Technol.*, *33*(2), 329–336, doi:10.1021/es980374g.
- Kirchstetter, T. W., B. C. Singer, R. A. Harley, G. R. Kendall, and M. Traverse (1999b), Impact of California reformulated gasoline on motor vehicle emissions. I. Mass emission rates, *Environ. Sci. Technol.*, *33*(2), 318–328, doi:10.1021/es9803714.
- LaFranchi, B. W., A. H. Goldstein, and R. C. Cohen (2011), Observations of the temperature dependent response of ozone to NO_x reductions in the Sacramento, CA urban plume, *Atmos. Chem. Phys.*, *11*(14), 6945–6960, doi:10.5194/acp-11-6945-2011.
- Lawson, D. R. (1990), The Southern California Air-Quality Study, *J. Air Waste Manage. Assoc.*, *40*(2), 156–165.
- Mayrsohn, H., M. Kuramoto, J. H. Crabtree, R. D. Sothorn, and S. H. Mano (1975), Atmospheric hydrocarbon concentrations: June–September, 1975, report, State of Calif. Air Resour. Board, Sacramento.
- Murphy, J. G., D. A. Day, P. A. Cleary, P. J. Woodriddle, D. B. Millet, A. H. Goldstein, and R. C. Cohen (2007), The weekend effect within and downwind of Sacramento - Part I: Observations of ozone, nitrogen oxides, and VOC reactivity, *Atmos. Chem. Phys.*, *7*(20), 5327–5339, doi:10.5194/acp-7-5327-2007.
- Neligan, R. E. (1962), Hydrocarbons in the Los Angeles atmosphere—A comparison between the hydrocarbons in automobile exhaust and those found in the Los Angeles atmosphere, *Arch. Environ. Health*, *5*(6), 581–591.
- Nowak, J. B., et al. (2004), Gas-phase chemical characteristics of Asian emission plumes observed during ITCT 2K2 over the eastern North Pacific Ocean, *J. Geophys. Res.*, *109*, D23S19, doi:10.1029/2003JD004488.
- Parrish, D. D., M. Trainer, D. Hereid, E. J. Williams, K. J. Olszyna, R. A. Harley, J. F. Meagher, and F. C. Fehsenfeld (2002), Decadal change in carbon monoxide to nitrogen oxide ratio in U.S. vehicular emissions, *J. Geophys. Res.*, *107*(D12), 4140, doi:10.1029/2001JD000720.
- Parrish, D. D., H. B. Singh, L. Molina, and S. Madronich (2011), Air quality progress in North American megacities: A review, *Atmos. Environ.*, *45*(39), 7015–7025, doi:10.1016/j.atmosenv.2011.09.039.
- Renzetti, N. A. (1956), Ozone in the Los Angeles atmosphere, *J. Chem. Phys.*, *24*, 909, doi:10.1063/1.1742639.
- Schauffler, S. M., E. L. Atlas, D. R. Blake, F. Flocke, R. A. Lueb, J. M. Lee-Taylor, V. Stroud, and W. Travnicek (1999), Distributions of brominated organic compounds in the troposphere and lower stratosphere, *J. Geophys. Res.*, *104*(D17), 21,513–21,535, doi:10.1029/1999JD900197.
- Schmid, H., E. Pucher, R. Ellinger, P. Biebl, and H. Puxbaum (2001), Decadal reductions of traffic emissions on a transit route in Austria—Results of the Tauerntunnel experiment 1997, *Atmos. Environ.*, *35*(21), 3585–3593, doi:10.1016/S1352-2310(00)00568-9.
- Sommariva, R., J. A. de Gouw, M. Trainer, E. Atlas, P. D. Goldan, W. C. Kuster, C. Warneke, and F. C. Fehsenfeld (2011), Emissions and photochemistry of oxygenated VOCs in urban plumes in the northeastern United States, *Atmos. Chem. Phys.*, *11*(14), 7081–7096, doi:10.5194/acp-11-7081-2011.
- Stemmler, K., S. Bugmann, B. Buchmann, S. Reimann, and J. Staehelin (2005), Large decrease of VOC emissions of Switzerland's car fleet during the past decade: Results from a highway tunnel study, *Atmos. Environ.*, *39*(6), 1009–1018, doi:10.1016/j.atmosenv.2004.10.010.
- Thornton, J. A., et al. (2002), Ozone production rates as a function of NO_x abundances and HO_x production rates in the Nashville urban plume, *J. Geophys. Res.*, *107*(D12), 4146, doi:10.1029/2001JD000932.
- von Schneidemesser, E., P. S. Monks, and C. Plass-Duelmer (2010), Global comparison of VOC and CO observations in urban areas, *Atmos. Environ.*, *44*(39), 5053–5064, doi:10.1016/j.atmosenv.2010.09.010.
- Warneke, C., et al. (2007), Determination of urban volatile organic compound emission ratios and comparison with an emissions database, *J. Geophys. Res.*, *112*, D10S47, doi:10.1029/2006JD007930.
- Warneke, C., et al. (2011), Airborne formaldehyde measurements using PTR-MS: Calibration, humidity dependence, inter-comparison and initial results, *Atmos. Meas. Tech.*, *4*(10), 2345–2358, doi:10.5194/amt-4-2345-2011.
- Winer, A. M., J. W. Peters, J. P. Smith, and J. N. Pitts (1974), Response of commercial chemiluminescent NO-NO₂ analyzers to other nitrogen-containing compounds, *Environ. Sci. Technol.*, *8*(13), 1118–1121, doi:10.1021/es60098a004.