

# Light-Duty Vehicle Emissions and Urban Air Quality: Past, Present, and Future Perspectives

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## Abstract

A perspective on past, present, and future light-duty vehicle emissions and urban air quality is provided. In conjunction with engine advancements, automotive fuel composition has been fine tuned to balance efficiency and power demands while minimizing emissions. Pollutant emissions from internal combustion engines result from complex processes involving interactions between the fuel and engine parameters. Engine hardware and operating conditions, after-treatment catalysts, and fuel composition all affect the amount and composition of emissions leaving the vehicle tailpipe. While engine and after-treatment effects are generally larger than fuel effects, engine and after-treatment hardware can require specific fuel properties. Consequently, the best prospects for achieving the highest efficiency and lowest emissions lie with optimizing the entire fuel–engine–after-treatment system. Vehicle emissions consist of volatile organic compounds (VOCs), CO, nitrogen oxides (NO<sub>x</sub>), and particulate matter (PM). VOCs, NO<sub>x</sub>, and PM contribute to photochemical smog in urban atmospheres. The past few decades have seen large reductions in the emissions of NO<sub>x</sub>, VOCs, and particulate matter (PM) emissions from new vehicles. This reduction of emissions from traffic has been an important factor in improvements in the air quality in many U.S. and European cities.

**Keys-words:** light-duty vehicle (LDV) emissions, air quality, historical trends

## 1 Introduction

Throughout human history, urban areas have been associated with high levels of population density, economic activity, emissions and air pollution. Serious urban air pollution in antiquity is well documented (Heidorn, 1978; Brimblecombe,

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1995; Makra, 2015). Seneca in AD 61 noted the need to escape the gloomy smoke and kitchen smells of Rome (Heidorn, 1978; Makra, 2015). In 1273 the first smoke abatement law was enacted in London (Heidorn, 1978). In 1573 Elizabeth I complained about smoke from coal in London. In the 1870s-1950s severe air pollution episodes associated with the burning of coal were typical in London in the winter. The London physician Harold Des Veaux is credited with using the word “smog” in 1905 derived from a combination of the words smoke and fog to describe air pollution. In the 1940s Los Angeles suffered serious air pollution episodes. In the early 1950s it was recognized by Haagen-Smit and coworkers that the nature of the air pollution in Los Angeles was fundamentally different from that in London. It was shown that photochemical reactions involving nitrogen oxides and volatile organic compounds (VOCs) generated ozone which was a major component of the air pollution in Los Angeles (Haagen-Smit 1951; Haagen-Smit et al. 1952). The reactions are complex, but can be represented in simple form by the mechanism in Figure 1 (Wallington et al., 2006; Calvert et al., 2015).

VOCs and nitrogen oxides (NO<sub>x</sub>) are emitted in vehicle exhaust and from other sources. VOCs react with hydroxyl radicals in the atmosphere to produce alkyl radicals which rapidly add O<sub>2</sub> to give alkylperoxy radicals (RO<sub>2</sub>). The dominant fate of alkylperoxy radicals in urban air is reaction with NO to give NO<sub>2</sub> and alkoxy radicals. The alkoxy radicals react to give oxygenated VOCs which can then produce more alkyl peroxy radicals as indicated in the left hand cycle in Figure 1. NO<sub>2</sub> has a lifetime of the order of minutes in the sunlit atmosphere and undergoes photolysis to reform NO and generate oxygen atoms and hence ozone as indicated in the right hand circle in Figure 1. Recognition of the contribution of vehicle emissions to urban air quality issues has led to increasingly stringent regulations over the past few decades around the world to control vehicle emissions (Johnson, 2016).

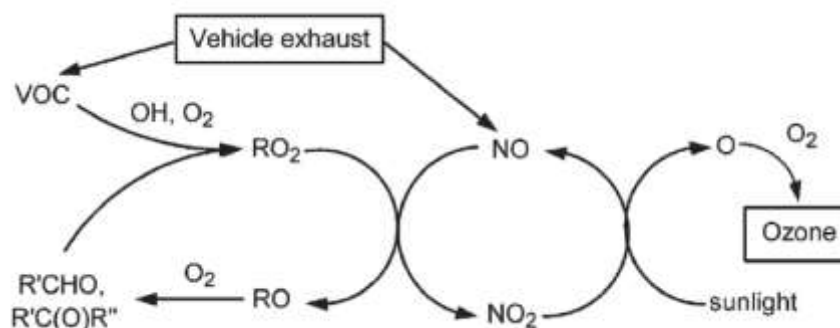


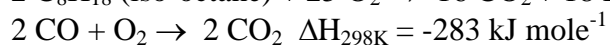
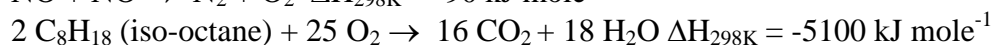
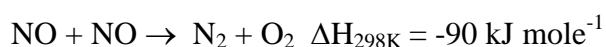
Figure 1: Photochemical production of ozone, reproduced from Wallington et al. (2006) with permission from the Royal Society of Chemistry.

There has been a strong and consistent trend of urbanization over the past century and this trend is expected to continue over the coming decades. The United

Nations estimated that in 2015 approximately 4.0 billion people, 54% of the world's population, lived in urban areas and by 2030 these figures will rise to 5.1 billion, 60%, (UN Population Division, 2014). With increasing urban population and increasing vehicle population it is important to understand the trends of vehicle emissions and urban air quality.

## 2 Light-duty vehicle emissions

Exhaust from internal combustion engines contains volatile organic compounds (VOCs), CO, nitrogen oxides (NO<sub>x</sub>), and particulate matter (PM). VOCs and NO<sub>x</sub> form photochemical smog in urban atmospheres, CO and PM may have adverse health impacts. Reduction of VOC, NO<sub>x</sub>, CO, and PM emissions from vehicles and from other sources is needed to address local air pollution. Modern internal combustion engines are remarkably efficient and the majority of the fuel is combusted to CO<sub>2</sub> and H<sub>2</sub>O within the approximately 40-100 ms the air/fuel mixture is in the engine. VOC emissions are unburnt or partially burnt fuel. CO is partially burnt fuel. Particulate matter emissions stem from oxygen deficient combustion and from pyrolysis of fuel droplets. NO<sub>x</sub> is mainly formed by the Zeldovich mechanism which is initiated by thermal dissociation of oxygen molecules to give oxygen atoms which react with molecular nitrogen to produce NO (Zeldovich, 1946). Engine design and control strategies are employed to maximize the combustion efficiency (conversion of fuel into CO<sub>2</sub> and H<sub>2</sub>O) and minimize the formation of NO, CO, and soot in the engine (Wallington et al., 2006; Johnson, 2016). From the viewpoint of treating vehicle exhaust it is very fortunate that thermodynamics favor the conversion of NO, VOCs, CO, and soot into more environmentally benign compounds as indicated below.



While the above reactions are thermodynamically favored, they are too slow to remove the pollutants before the exhaust leaves the vehicle tailpipe. Catalysts are used in vehicle emission control systems to catalyze the oxidation of VOCs, CO, and soot into CO<sub>2</sub> and H<sub>2</sub>O and the reduction of NO (Twigg, 2007). It is a challenging engineering task to design vehicle emission control systems which can complete both oxidation and reduction reactions under a range of operating temperatures and which are efficient for the life of the vehicle. However, systems have been developed which offer very effective control of vehicle emissions (Wallington et al., 2006; Twigg, 2007; Johnson, 2016). Catalytic converters used in gasoline vehicles consist typically of one or more monolithic ceramic

honeycomb substrates surrounded by a mounting material and housed in a metal can. The monolith surface is coated with alumina, other high surface area oxides such as ceria or zirconia, and the platinum group metals Pt, Rh, and Pd. The precious metals facilitate catalytic reduction/oxidation of the pollutants in the exhaust gas, while the reducible oxides can improve catalytic efficiency by storing and releasing oxygen as engine operating conditions change.

Automotive catalysts are very efficient after the catalyst reaches its operating temperature (light-off). Oxidation catalysts were introduced in the mid-1970s to control HC and CO emissions. When more stringent  $\text{NO}_x$  control was mandated, a new type of catalyst was required that could oxidize CO and HC to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  while simultaneously reducing  $\text{NO}_x$  to  $\text{N}_2$ . This type of catalyst is designated “three-way” because it controls the emissions of three regulated emissions; CO, HC, and  $\text{NO}_x$ . To meet the requirement of simultaneously oxidizing CO and HC while reducing  $\text{NO}_x$ , the engine must be operated close to the stoichiometric air/fuel ratio where the amount of  $\text{O}_2$  in the air matches that required to fully combust the fuel. This requires careful feedback control using an on-board exhaust gas oxygen sensor. The overall conversion efficiency is improved by oscillating the air/fuel ratio by about ~2-3% around the stoichiometric value (Wallington et al., 2006). Figure 2 shows the fine honeycomb structure of a typical catalyst. Figure 3 illustrates the efficiency of such catalysts at removing total hydrocarbons (THC), carbon monoxide, and  $\text{NO}_x$ .

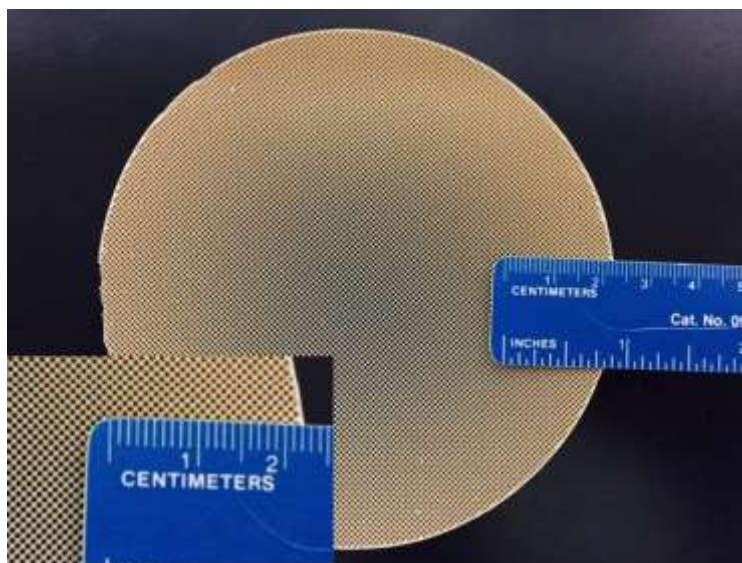


Figure 2: Typical catalyst monolith used in modern gasoline vehicles showing the fine honeycomb channels through which the exhaust passes.

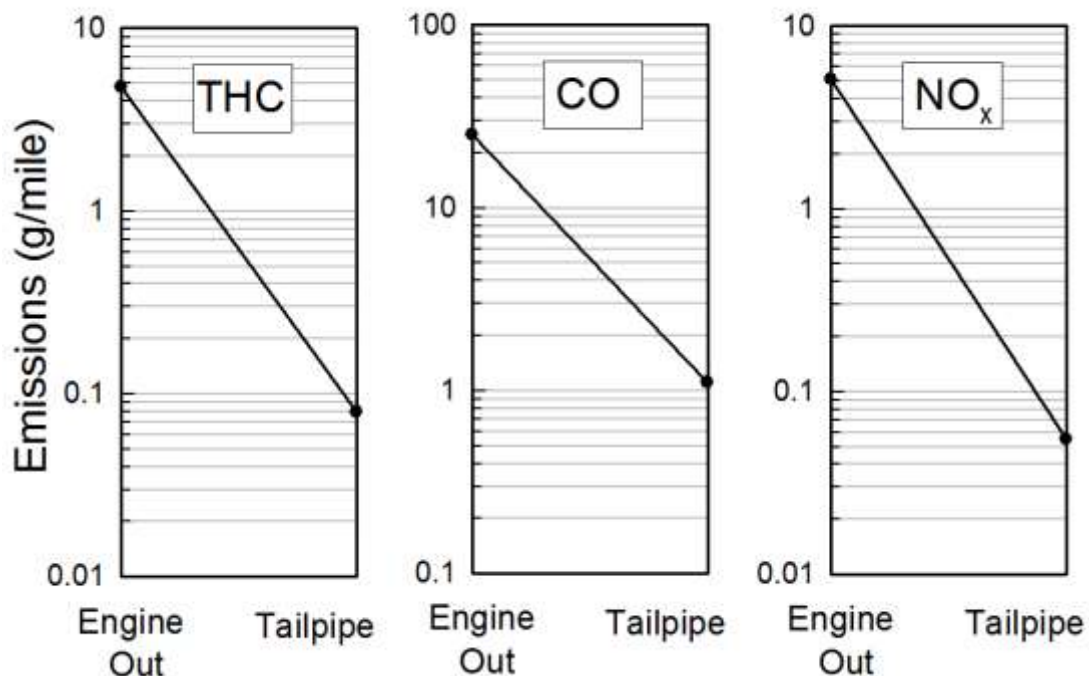


Figure 3: Plots of engine-out and tailpipe total hydrocarbon, CO, and NO<sub>x</sub> for a gasoline vehicle measured over the FTP cycle illustrating the efficiency of the emission control system. Data were taken from Hubbard et al. (2014).

In contrast to gasoline vehicles which operate at, or close to, stoichiometry, diesel engines operate lean. Diesel exhaust consists mainly of N<sub>2</sub>, O<sub>2</sub> (typically approximately 8-10%, but can be as high as 20% during idle, or as low as 6% during filter regeneration), CO<sub>2</sub>, and H<sub>2</sub>O. Diesel engines generally have lower NO<sub>x</sub> and VOCs emissions and higher PM emissions than gasoline engines. Diesel particulate filters are used to treat PM. Diesel exhaust contains a significant amount of O<sub>2</sub> and it is not possible to use three way catalysts to remove NO<sub>x</sub> from diesel exhaust. The technology used to treat NO<sub>x</sub> in diesel exhaust is either lean NO<sub>x</sub> traps (LNTs) or selective catalytic reduction (SCR). In LNTs the NO<sub>x</sub> is trapped during lean operation and reduced in rich transients. In SCR systems ammonia is used to selectively reduce NO<sub>x</sub> over a Cu/zeolite catalyst. Figure 4 shows a schematic which illustrates how a diesel oxidation catalyst, selective catalytic reduction technology, and diesel particulate filter can be combined together into an emission control system for a modern diesel vehicle. As evident from Figure 4, the emission system is complex and needs to be designed as a system.

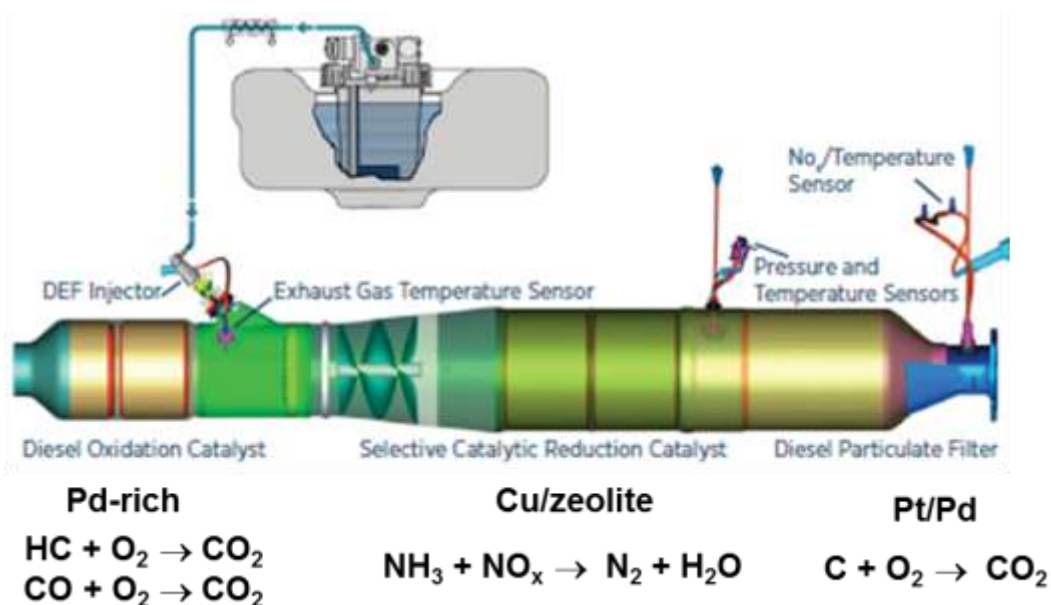


Figure 4: A schematic showing a typical emission control system for a diesel vehicle in the U.S. The exhaust flows from left to right. A Pd-rich DOC catalyzes the oxidation of hydrocarbons and CO, diesel exhaust fluid (DEF, a solution of urea in water) is injected into the exhaust, urea decomposes to give ammonia which is used to selectively reduce NO<sub>x</sub> over a Cu/zeolite catalyst, finally soot is oxidized using a Pt/Pd catalyst in the diesel particulate filter.

### 3 Light-duty vehicle emission trends

The Coordinating Research Council has funded a series of field measurements in which remote sensing techniques have been used to measure emissions from the on road light-duty vehicle fleet in Chicago. Non-dispersive IR spectroscopic monitoring techniques were used for CO, CO<sub>2</sub>, and HC and dispersive UV spectroscopic monitoring techniques were used for NO and NO<sub>2</sub>, SO<sub>2</sub> and NH<sub>3</sub>. Measurements were conducted in 1997, 1998, 1999, 2000, 2002, 2004, 2006, and 2014 with approximately 20,000 vehicles measured in each study (Bishop and Stedman, 2015). Figure 5 shows the median and the mean concentrations of CO, NO, and hydrocarbons (HC) in the exhaust from the on-road fleets in 1997-2014. As seen from Figure 5 there has been a large decrease in the levels of CO, NO, and HC in LDV exhaust over the past 20 years. There is a significant difference between the median and mean values in Figure 5 showing the skewed nature of the distribution. The percent of emissions contributed by the highest emitting 1% of the fleet (the 99<sup>th</sup> percentile) increased substantially between 1997 and 2014 and in 2014 stood at approximately 25%, 35%, and 42% for NO, CO, and HC, respectively (Bishop and Stedman, 2015).

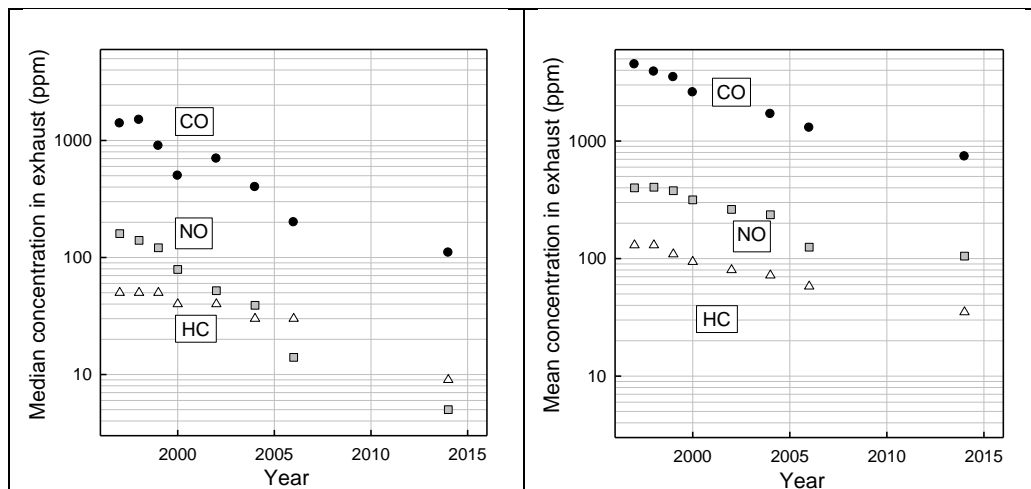


Figure 5: Median and mean concentrations of CO (filled circles), NO (gray squares), and HC (open triangles) determined by remote sensing of on-road automobile emissions in the Chicago area (Bishop and Stedman, 2015).

Another example of the progress made in reducing vehicle emissions comes from the experience in Beijing. Zhang et al. (2014) have assessed the emissions from the on-road vehicle fleet in Beijing from 1998 to 2013. Interestingly, as seen in Figure 6, despite a large increase in the total on-road vehicle fleet in Beijing there is a trend of decreasing emissions from the on-road fleet. This trend reflects the retirement of old vehicles and the introduction of new vehicles with modern emission control systems into the fleet.

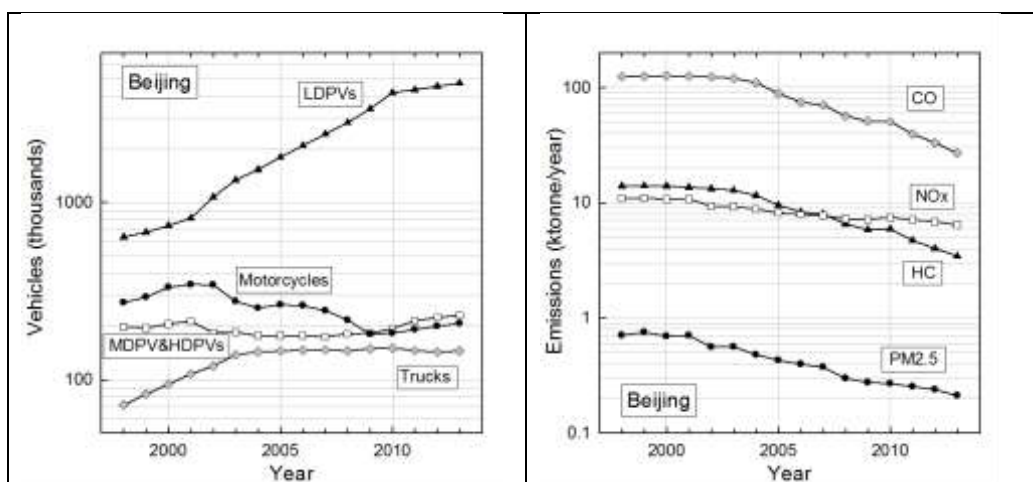


Figure 6: Left hand panel: Fleet of light-duty passengered vehicles (LDPVs), motorcycles, medium-duty and heavy-duty passenger vehicles (MDPVs & HDPVs), and trucks. Right hand panel: the total on-road emissions of CO (gray diamonds), NO<sub>x</sub> (open squares), HC (filled triangles), and PM<sub>2.5</sub> (filled circles) in Beijing, China. Data were taken from Zhang et al. (2014).

## 4 Air quality trends

Figure 7 shows concentrations of O<sub>3</sub>, CO, PM<sub>2.5</sub>, Pb, SO<sub>2</sub> and NO<sub>2</sub> air pollutants in cities in the U.S. from 1980 to 2014. As illustrated in Figure 7, urban air quality in U.S. cities has improved substantially over the past 35 years. There is a substantial downward trend in the levels of all these air pollutants. The improvements seen in Figure 7 are even more impressive when the large increases in population, economic activity, and vehicle miles traveled over the same period are considered. The horizontal dashed lines in the panels in Figure 7 are the National Ambient Air Quality Standards (NAAQS) in the United States: 4<sup>th</sup> maximum 8-hour average [O<sub>3</sub>], 70 ppb; 2<sup>nd</sup> maximum 8-hour average [CO], 9 ppm; seasonally weighted annual average PM<sub>2.5</sub>, 12 µg m<sup>-3</sup>; annual maximum 3-month average [Pb], 0.15 µg m<sup>-3</sup>; annual 99<sup>th</sup> percentile of daily maximum 1-hour average [SO<sub>2</sub>], 75 ppb; and annual average [NO<sub>2</sub>], 21 ppb (U.S.E.P.A., 2016). Levels of CO, PM<sub>2.5</sub>, Pb, SO<sub>2</sub>, and NO<sub>2</sub> in the air in U.S. cities are generally below the NAAQS. The decreases in the ambient concentrations of the pollutants shown in Figure 7 reflects progress made in reducing the emissions from vehicles and other sources in urban areas. While there has been great progress in improving air quality there are challenges in meeting some of the air quality standards. This is perhaps best illustrated by the top left panel of Figure 7 which shows the challenge of meeting the new ozone NAAQS of 70 ppb. There are also significant challenges in meeting the PM<sub>2.5</sub> standard in many areas. In total approximately 57 million people in the U.S. live in regions which violate at least one of the NAAQS (U.S.E.P.A., 2016).

As in the U.S., major improvements in air quality have been made in cities in Europe. European cities such as London have historically suffered from severe air pollution associated with the burning of solid fuels, wood and later coal, for heating and cooking. In the late 19<sup>th</sup> and early 20<sup>th</sup> centuries London was known for its pea-souper fogs with visibility in severe episodes reduced to a few meters. The enactment of regulations restricting emissions and the development of technologies with low emissions led to dramatic improvements in the air quality. As an example, in the December 1952 London smog episode concentrations of smoke and SO<sub>2</sub> both peaked at approximately 4000 µg m<sup>-3</sup> (Greater London Authority, 2002); current levels of PM<sub>10</sub> and SO<sub>2</sub> in London are 15-35 µg m<sup>-3</sup> and 2-5 µg m<sup>-3</sup>, respectively (King's College London, 2016). The air quality in European cities such as London is probably the best that it has been in centuries. Despite the dramatic improvements the current air quality still falls short of European standards in many cities. In 2013 approximately 17%, 15%, and 9% of the EU-28 urban population was exposed to PM<sub>10</sub> levels, O<sub>3</sub>, and NO<sub>2</sub> concentrations, respectively, above the European limit values (European Environment Agency, 2015). It should be noted that as shown in the bottom right hand panel in Figure 6, the European annual average limit value for NO<sub>2</sub> of 40 µg m<sup>-3</sup> (21 ppb) is more than a factor of 2 more stringent than the corresponding



NAAQS in the U.S. of 53 ppm.

Addressing the air quality challenges in Europe will require reduction in emissions from traffic and from other sources in urban areas. The challenge associated with bringing roadside air quality monitoring stations in Germany is addressed in detail by Toenges-Schuller et al. (2016) in this issue. Toenges-Schuller et al. (2016) estimate that the fraction of traffic-influenced stations exceeding the air quality limit for annual mean NO<sub>2</sub> is expected to be reduced from about 50% in 2015 to between 1% and 4% in 2030. Meeting the European standards for PM<sub>10</sub> and O<sub>3</sub> will be challenging because of the stringency of the standards and the diversity of precursor emission sources. The emissions of NO<sub>x</sub>, VOCs, CO, and PM from traffic have declined substantially over the past 20-30 years and we are witnessing a transition from a situation where it was clear that traffic was the dominant source of emissions to one where traffic is no longer the dominant source of emissions. This is illustrated in the plot in Figure 8 showing the evolution of VOC emissions in EU-27 from 1990 to 2010. In 1990 it was clear that cars were the dominant source of VOC emissions. Over the 20 years to 2010 the emissions of VOCs from cars decreased by a factor of approximately 7 and there has been a large shift in the relative importance of the different emission sources. The data in Figure 8 are national not urban emissions and it needs to be recognized that because of the proximity of vehicles, emissions from vehicles can lead to more significant human exposure than from some other emission sources.

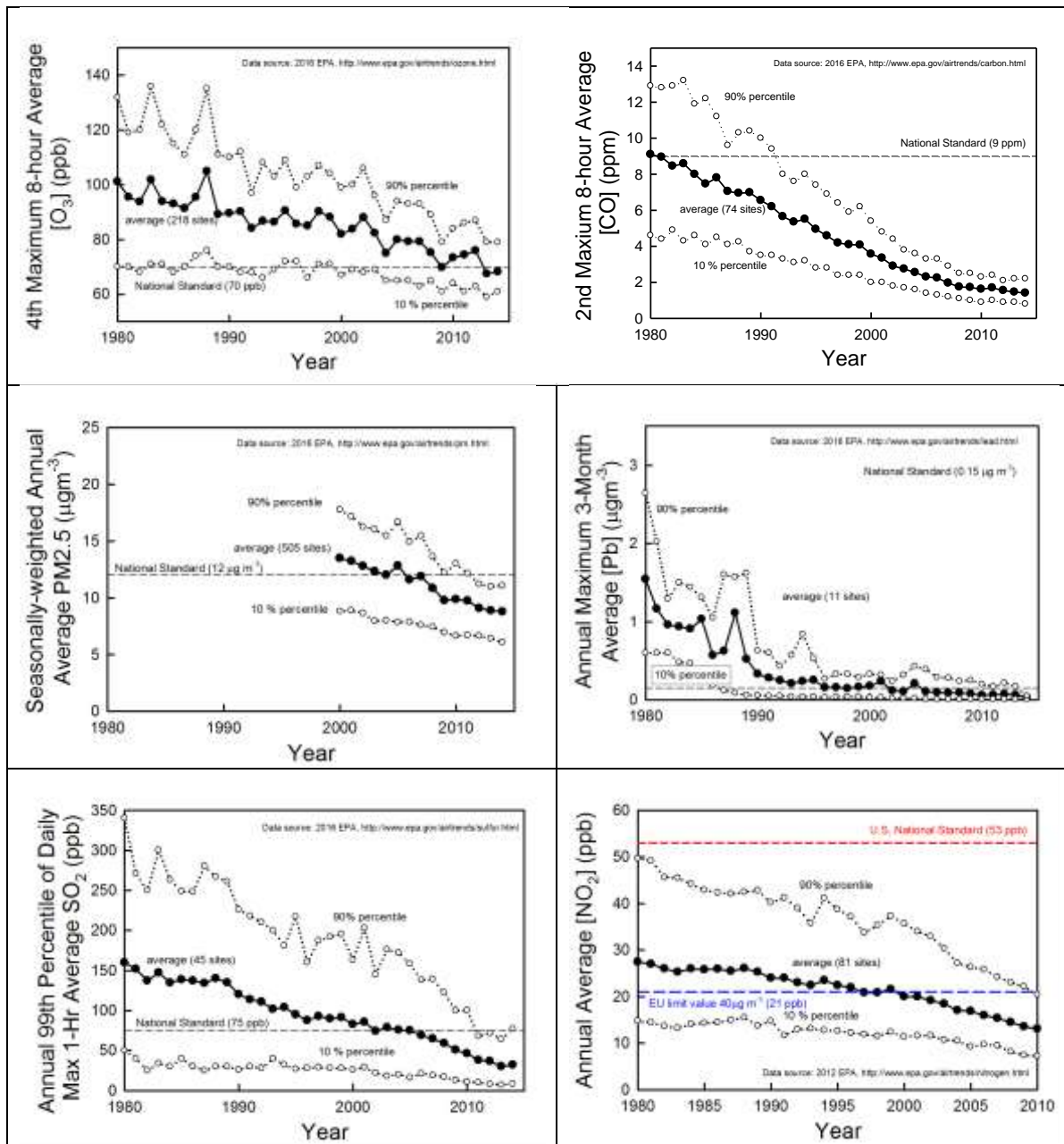


Figure 7: Trends in concentrations of  $O_3$ ,  $CO$ ,  $PM_{2.5}$ ,  $Pb$ ,  $SO_2$ , and  $NO_2$  based on data from 218, 74, 505, 11, 45, and 81 sites, respectively, in U.S. cities. The solid circles are average values, the open circles show the 10<sup>th</sup> and 90<sup>th</sup> percentile values (U.S.E.P.A. database, <https://www3.epa.gov/airtrends/aqtrends.html>).

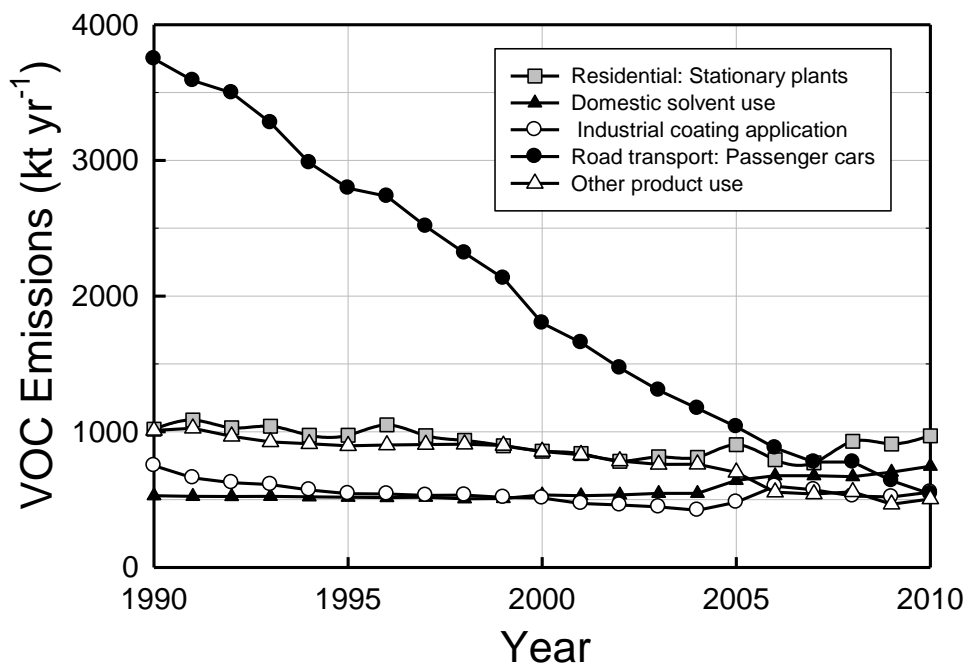


Figure 8. VOC emissions in EU-27 from 1990 to 2010, data from European Environment Agency (2012), reproduced from Calvert et al. (2015) with permission from Oxford University Press.

## 5 Conclusions

Air quality issues have been important for a very long time and will continue to be important for the foreseeable future. Urbanization and industrialization over the past century have heightened the challenges posed by air quality.

Great progress has been made in reducing emissions of VOCs, NO<sub>x</sub>, CO, and PM from vehicles. Urban air quality has improved substantially over the past 50 years in the U.S. and Europe. The trend of decreased emissions from traffic will continue over the coming decades. We are in the midst of a fundamental shift in the relative importance of traffic emissions versus emissions from other sources with traffic emissions becoming less important in many urban areas.

Many urban centers especially those in developing countries currently have air pollution challenges. Vehicle emissions in developing countries are likely to decrease substantially in the coming decades. Many sources of air pollution will need to be addressed to meet the future air quality goals. Experience in developed countries offers hope for the future in developing countries.

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